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FINAL REPORT

**THE EFFECTS OF TOXIC CONTAMINANTS IN WATERS
of the SAN FRANCISCO BAY and DELTA**

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EXECUTIVE SUMMARY

This report summarizes current information regarding the effects of toxic contaminants on aquatic resources in the San Francisco Bay and Delta. Evidence for impacts in Bay and Delta waters as well as in tributary watersheds was examined. Sources of contaminants include both point and nonpoint sources. Point sources include cooling discharges, as well as industrial and municipal effluents. Nonpoint sources include agricultural runoff, tailing from abandoned mining sites, and urban stormwater discharges.

Direct evidence for toxicity in waters of the Bay-Delta complex comes from toxicity tests conducted on these waters with endemic species as well as laboratory surrogate species. Using such tests, toxicity has been demonstrated on a regular basis. In many samples, the chemical(s) responsible for toxicity was identified. In addition to identifying numerous pesticides, notably diazinon, chlorpyrifos, malathion, methyl parathion, and carbofuran as the primary cause of toxicity in the Sacramento River, metals were found to be a major contributor of toxicity as well.

Many of the point and nonpoint source inputs in the system also exhibited toxicity. Pesticides, particularly diazinon and chlorpyrifos, as well as metals, were among the causes of toxicity identified.

Seasonal patterns in toxicity, particularly related to precipitation events and agricultural practices, also emerged. The frequency of toxicity often increased during and immediately after precipitation events. In these events, runoff washed pesticides from agricultural applications, metals from mining sites, and a variety of contaminants from urban areas into receiving waters. Agricultural practices often resulted in large quantities of pesticides being applied in a relatively short period. A proportion of the applied amount can be moved offsite either due to precipitation or as tailwater from irrigation.

Other evidence for toxicity comes from measured residues or body burdens in resident organisms, particularly birds and fish. In some cases, levels of contaminants such as

chlorinated hydrocarbons and selenium reached or exceeded levels that have been shown to cause adverse effects elsewhere. For a few species in the Bay, reproductive effects have been demonstrated that are consistent with these concentrations.

Additional evidence for the potential of adverse effects comes from chemical analytical data. Based on analyses of hundreds of water samples, concentrations of diazinon and chlorpyrifos are frequently at levels that exceed those determined to be safe for aquatic life. These exceedences are particularly apparent in Delta waters and tributaries, along with urban stormwater following precipitation events. The concentrations of selected metals also exceed water quality criteria values on an intermittent basis.

Overall, this review suggests that contaminants reach toxic concentrations on a widespread basis throughout the Bay/Delta complex, although the frequency and identity of the contaminant(s) may vary on a seasonal basis. Based on studies conducted in other watersheds that yielded similar data, one would expect impacts on local aquatic resources. This expectation is consistent with widespread declines of many species of fish and invertebrates, particularly in the Delta and its tributaries. Both the direct evidence of toxicity and analytical evidence support the potential for adverse effects and strongly suggests that contaminants should be taken into account in any plan aimed at recovering aquatic resources in the system. Although many argue that water is the primary factor controlling populations in the Delta, the complex interactions between contaminants and water (water acts as a dilution medium) and the likelihood of declining water availability in the future suggests that contaminants may play an important role in limiting the Delta's recovery in spite of reduced water exports. Failure to take contaminants into the equation may undervalue the role of reduced water exports. Furthermore, if contaminants were reduced, less flow would be necessary to maintain water quality and outflow requirements could be based solely on biological needs.

INTRODUCTION

The San Francisco Bay and Delta is located at the confluence of the Sacramento and San Joaquin Rivers. The Delta itself comprises over 700 miles of interconnected waterways and encompasses 1153 square miles (State Lands Commission 1991). Historically, the area was rich in wildlife resources, including large mammals such as bear, antelope, deer, elk, and other mammals. Waterfowl and fish species were also diverse and abundant. However, most of the marshlands have been developed for agricultural (92 percent of original Delta wetlands have been converted to agriculture) and urban uses. Subsequent modifications of water flow patterns to facilitate water exports and flood control have dramatically altered the morphology and probably the carrying capacity of the Delta. Coincidentally, most of the wildlife resources have declined precipitously or disappeared altogether (State Lands Commission 1991). For example, of 29 indigenous species of fish, 12 have been either eliminated from the Delta or are currently threatened with extinction. Local declines or near extirpation have been shown for populations of several bird species, California sea lion, tiger salamander, red-legged frog, giant garter snake, and western pond turtle (SFEP 1993).

Potential impacts related to declines of species include habitat modifications, altered flow patterns, water exports, and introductions of new species (State Lands Commission 1991). Habitat modifications include the diking and drainage of former wetlands, as well as alteration of existing channels. These activities reduce or eliminate habitat, particularly the important spawning and nursery areas often associated with seasonally or tidally flooded vegetation, and eliminate sources of nutrients. Levee construction and channel modification reduce the riparian habitat and alter flows in the channels. The altered flow patterns may then upset migration patterns and make local conditions unsuitable for some organisms. In addition, dredging may also resuspend toxic contaminants present in the sediments.

On a larger scale, control of run-off by upstream dams has reduced the frequency and extent of inputs historically associated with rain and snowmelt runoff. This in turn reduces organic and inorganic inputs into the Delta and reduces the flows available for those species that depend on "high water" for spawning and migration. Water exports are considerable, often exceeding 50

percent of the Delta outflow, and comprise up to 10 million acre feet annually. These exports alter flow patterns and permanently export nutrients, algae, invertebrates, and early life history stages of fish from the system.

Finally, introduced species may supplant local species either by direct competition or by being better adapted to the altered conditions in the Estuary than species historically found there. Examples of declining aquatic biota in the Bay-Delta are presented below (SFEP 1993).

- Only 8 percent of the historic tidal wetlands remain.
- Phytoplankton abundance has decreased.
- Zooplankton abundance has decreased.
- Chinook salmon stocks have decreased an average of 70%; San Joaquin stocks have been reduced by over 90 percent and the Sacramento winter-run is a state and federally listed species.
- The striped bass population has decreased to less than 20 percent of its numbers in the 1960s.
- The once-abundant Delta smelt is now a federally listed species.
- Other species of fish, including Sacramento splittail, white catfish, and longfin smelt have also declined dramatically.

In addition to the factors described above, contaminants have also been suggested as contributing to the decline of Bay and Delta resources (SFEP 1993). At least 65 pollutants have been identified as entering the Estuary at an annual rate of 5 to 40,000 tons each. Point and non-point sources are implicated, along with dredging, spills, and atmospheric deposition. The problem is widespread throughout the system, but localized hotspots may be associated with point source dischargers, marinas, harbors, and industrial waterways. SFEP (1993) points out that trace contaminants may be concentrated to high levels in animal tissues and that bioassays of effluents, sediments, and ambient water have demonstrated toxicity. Although there are some instances in which adverse effects have been demonstrated in local populations, notably starry flounder and black-crowned night herons, the impact of toxic contaminants on the behavior, population dynamics, and community structure of organisms inhabiting the Estuary are poorly understood (SFEP 1993).

The major objective of this report is to summarize current knowledge regarding the potential effects of toxicants on organisms that inhabit the San Francisco Bay and Delta. It encompasses studies conducted in the Estuary and, based on knowledge gained from other systems, also describes potential effects that are not yet documented in the Estuary. It also makes recommendations to focus further research in areas for which the data are currently insufficient to support conclusions.

The report is divided into sections in order to present the material manageably. The first section summarizes the findings of previous works that have compiled data on contaminants in this system. Evidence of toxicity in samples collected from ambient waters associated with the Bay and Delta is presented next, since this is potentially the strongest evidence that contaminants are present at levels that result in adverse effects. This is followed by a summary of impacts from non-point sources, which include agricultural and urban stormwater inputs into the Bay-Delta system. In some cases, such as the Colusa Basin Drain (CBD), agricultural sources constitute large identifiable inputs into the system. Conversely, numerous small agricultural drains and return pumps contribute to waterways throughout the system. Urban stormwater inputs are similar in that they often comprise most of the high flows of local creeks and storm channels, but the inputs are diffuse and may not be readily treatable.

Next, toxicity and contributions from point source dischargers are reviewed. These dischargers include publicly owned sewage treatment works (POTWs), industrial dischargers, and oil refineries. Any toxicity associated with these discharges is compared to the potential for the receiving water to dilute toxic components to levels below those associated with adverse effects.

The section that describes species effects deals with data directly related to the Bay/Delta system, as well as data on the same species found in different systems. This is because data which demonstrate effects of contaminants on organisms that inhabit the Bay and Delta are limited, and it is helpful to have information gathered in other studies to use as a basis for generating data that can be applied locally. These data may help identify key species and parameters that can be incorporated into long term monitoring programs.

The Discussion synthesizes the information to address the potential for adverse effects of contaminants on the biota in the Bay/Delta system. Key points from the Discussion are presented in Conclusions and Recommendations which also identify data gaps that should be filled to provide a solid basis for generating decisions which deal with maintaining a productive estuary complex.

In general, the review was limited to studies and issues downstream of the City of Sacramento on the Sacramento River and Vernalis on the San Joaquin River. However, potential impacts and sources of contaminants upstream of these points were addressed if they pertained to species or processes thought to be of importance to the Estuary. In general, only water-borne contaminants and impacts were considered, although issues related to sediment were described if they were of particular importance or related to specific species of interest.

Information was gathered from a variety of sources. A comprehensive literature review was undertaken to identify recent publications in the peer-reviewed literature on areas of interest. Species of interest were identified through a briefing paper that described the biotic resources of the Bay and Delta (BDOC 1993). Citations found in the literature search were retrieved directly from library stacks, inter-library loans, or through literature retrieval services. Each article was then reviewed, summarized and included in this document as appropriate.

State agencies and university researchers were also contacted to determine whether pertinent unpublished reports or data were available. If available, these reports or data were reviewed, summarized and, where appropriate, included in this document.

To further ensure as much coverage as possible, draft copies of this document circulated through the various agencies and researchers for review, providing an additional opportunity to solicit comment and additional studies which may have been missed in the initial data screening process.

BACKGROUND

Significant efforts have been made in the past to document the status and trends of wildlife and aquatic resources and impacts and trends of toxic contaminants in Bay and Delta waters. These efforts include the substantial reviews prepared by the Aquatic Habitats Institute (Philips 1987; Gunther *et al.* 1987) and the San Francisco Estuary Project (SFEP 1993).

Philips (1987) reviewed toxic contaminants in the Bay-Delta complex and their possible biological effects. Major categories of contaminants included trace metals, selenium, organochlorines, and hydrocarbons. Sources included industrial and municipal dischargers, upstream inputs from agricultural and old mining sites, and urban stormwater discharges. It was pointed out that most of the studies investigating contaminants focused on monitoring concentrations rather than toxicity; thus it was difficult to actually demonstrate adverse impacts due to contaminants. This situation was exacerbated by the complex and highly variable Bay-Delta environment which induced substantial variability into the biological communities. Major findings included:

- Silver (Ag), copper (Cu), lead (Pb), zinc (Zn), chromium (Cr), mercury (Hg), cadmium (Cd), nickel (Ni), and tin (Sn) were found to be at elevated levels on a localized basis and also elevated in some organisms. Copper concentrations in the water at some locations exceeded EPA water quality criteria, and silver levels, particularly in the South Bay, were also of major concern.
- Mercury concentrations in some organisms reached levels of concern to human health and predators.
- Cadmium was not as ubiquitous as mercury, but was present in some organisms to levels that would be of concern to human health and mammalian predators.
- Selenium sources included the San Joaquin River and oil refineries. Elevated levels were found in sediment, water and biota on a localized basis.
- Chlorinated hydrocarbons, including pesticides and polychlorinated biphenyls (PCBs), were present in sediments at locally high concentrations. PCB and chlordane residues were of particular concern. PCB concentrations were also elevated in striped bass

compared to levels in striped bass from Coos Bay, Oregon, and in starry flounder and white croaker.

- Hydrocarbon contaminants arose primarily from the use, transport, and combustion of fossil fuels. Localized levels of sediment contamination occurred and large quantities were discharged to the water column via stormwater runoff along with industrial and municipal discharges. Both striped bass and starry flounder exhibited variable but elevated tissue concentrations of petroleum hydrocarbons.
- Prior to the 1960s and 1970s, poorly treated discharges from industrial and sewage outfalls significantly contaminated localized areas of the Bay and altered or eliminated local faunal assemblages. Improvement was noted by the early 1980s following implementation of more effective sewage treatment facilities.
- Concentrations of organochlorines were sufficiently high, particularly in localized areas, making adverse effects on biota likely, given their inherent toxicity and propensity to bioaccumulate. PCB concentrations were inversely related to spawning success of starry flounder. PCB concentrations may also have adversely affected reproductive success in local populations of Caspian terns, black-crowned night herons, and great blue herons. Fin erosion in fish species, including striped bass, was observed in fish collected in the vicinity of the Chevron Richmond Refinery outfall.
- Sediment toxicity was determined at a number of sites in the Bay with a variety of species. Only limited effluent toxicity data was available, but did suggest significant effects from point-source dischargers on Bay-Delta biota. Furthermore, wide variation was found in sensitivity between species, and short-term static tests were generally inappropriate indicators of effects. It was further recommended that this testing effort be expanded.

Gunther *et al.* (1987) assessed the loading of toxic contaminants to the Bay-Delta complex based on data collected between 1984 and 1986. Included in their evaluation were point sources, urban runoff, non-urban runoff, riverine inputs, dredged materials, atmospheric deposition, spills, and hazardous waste sites. The assessment included trace metals, chlorinated hydrocarbons, and petroleum-derived hydrocarbons. The major points were:

- In general, riverine (Sacramento and San Joaquin) inputs constituted the largest source of contaminants. However, these were often contained in large quantities of water, thus

effectively diluting the concentrations to comparatively low levels. Conversely, contaminants in point source and runoff sources were more concentrated and could reach levels of concern with respect to short-term toxicity.

- Arsenic, chromium, copper, and zinc inputs were dominated by riverine and non-urban runoff. Zinc was also present to a significant degree in urban runoff and a significant amount of chromium was discharged into Suisun Bay by one source.
- Cadmium, mercury, and nickel inputs were dominated by riverine inputs.
- Lead inputs were dominated by urban and non-urban runoff.
- Selenium and silver inputs were dominated by riverine and point sources (primarily oil refineries in the case of selenium and POTWs in the case of silver).
- Hydrocarbon inputs were dominated by urban runoff sources.
- Preliminary data suggested that PCB inputs were dominated by atmospheric deposition.
- Preliminary data suggested that polynuclear aromatic hydrocarbon (PAH) inputs were dominated by atmospheric deposition and urban runoff.
- During periods of low river flows, the relative importance of riverine inputs decreased.
- Dredging appeared to be a comparatively insignificant source of contaminants, but impacts may occur on a localized basis.
- Improved treatment and source control measures reduced concentrations of many trace contaminants from levels seen in the 1970s. For example, discharge of metals (cadmium, copper, chromium, lead, nickel, and zinc) from East Bay Municipal Utility District (EBMUD), the third largest POTW, averaged 790 kg/day in 1974 compared with 54 kg/day in 1986.

Montoya (1991) compiled the known sites of impaired water quality associated with toxic contaminants in the Delta. His data set encompassed the years 1976 to 1990 and was based on levels of known contaminants in the water column and sediments, tissue levels of known contaminants, and toxicity data. At least 80 percent of the freshwater that enters the Delta is from the Sacramento River, with the remainder primarily from the San Joaquin and Mokelumne Rivers. The Delta itself, as defined in Section 12220 of the Water Code, contains only about 2.7 percent of the entire Central Valley watershed. Approximately 70 percent of the land within the Delta is in agriculture. Montoya (1991) characterized sources of contaminants within the Delta as approximately 260 agricultural drains, 26 NPDES dischargers,

approximately 100 marinas, two major shipping ports, and 35,000 acres of urban land. The major findings follow:

- Metals concentrations (cadmium, copper, lead, and zinc) in both the Sacramento and San Joaquin Rivers were frequently above water quality criteria, particularly during the rainy season.
- Excessive selenium levels were seen in the lower San Joaquin River.
- Pesticide criteria were exceeded in several agricultural drains, the San Joaquin River, and the southeast Delta which is dominated by San Joaquin River flows.
- Tissue concentrations of DDT, PCBs, and toxaphene exceeded criteria values in the lower Sacramento and San Joaquin Rivers and Paradise Cut. Dieldrin concentrations exceeded criteria in the Sacramento River, and endosulfan and dicofol exceeded their criteria in the San Joaquin River and Paradise Cut.
- Mercury in tissue exceeded criteria in the Sacramento River.
- Dioxins were present in fish from the San Joaquin River at Antioch and in the Port of Stockton.
- Toxicity was found in both the Sacramento and San Joaquin Rivers, Cache Slough, Contra Costa Canal, and Steamboat Slough. Test organisms included water fleas (2 samples), echinoderm (1 sample), fathead minnows (24 samples) and striped bass larvae (3 samples). Most of the samples were collected from the Sacramento River during May and June in the years 1987 – 1989. [The reduced survival of fathead minnows, a comparatively robust laboratory test organism, should be of concern since many species exhibit much greater sensitivity.]
- Sediment criteria values were exceeded for PCB, chlordane, lindane, heptachlor, dieldrin and DDT in the Sacramento River at Rio Vista, Georgiana Slough, Mormon Slough, Mormon Channel, Morrison Creek, and the Stockton Turning Basin. PAHs exceeded sediment criteria in the Port of Stockton. Sediment criteria were exceeded at most Delta sites for chromium, copper, lead, mercury, nickel, and zinc; however, the metal criteria were based on saline bays so the levels may not reflect responses in Delta organisms. Sediment criteria for tri-n-butyl-tin (TBT) in salt water were exceeded at 3 of the 15 Delta marinas sampled.
- Both the San Joaquin and Sacramento Rivers export pesticides to the Delta. The impairments associated with the Sacramento River are of particular concern because of

the widespread distribution of Sacramento River water throughout the Delta.

Connor *et al.* (1993) summarized the results of bioassays on water samples collected in the Sacramento River Basin between 1988 and 1990. It was noted that at least 80 percent of the water entering the Delta came from the Sacramento River basin. The primary source of toxicants included agricultural discharges, mine drainage, urban run-off, and NPDES discharges. The study was conducted over a 2.5-year period to encompass a complete hydrologic cycle. Samples were collected approximately monthly from 25 different sites, including the Sacramento River from Lake Shasta to the Delta, the Feather and American Rivers, and various sloughs and agricultural drains. The EPA freshwater 3-species tests were used to assess toxicity. Significant findings include:

- A total of 414 samples were tested with fathead minnow larvae over 18 sampling events. Significantly reduced survival was observed in 38 samples. There was a strong seasonal component to toxicity, with most of the toxic samples collected between April and June. Samples from virtually all of the sites produced significant mortality during at least one testing event. Twelve additional samples produced significant reductions in growth. Over 12 percent of the samples produced toxicity to this species.
- A total of 368 samples were tested with *C. dubia* over 16 sampling events. Survival was significantly reduced in 88 samples. All of the sites exhibited reduced survival on at least two occasions and most of the toxicity was associated with the period between April and June. Twenty-nine additional samples reduced reproduction of this species. Collectively, over 30 percent of the samples produced toxicity to this species.
- A total of 335 samples were tested with algae. Growth was compared to that in samples collected from the Sacramento River at Colusa, which served as a "control". A total of 15 sampling events were conducted. Sixty-two samples produced reduced growth relative to the Colusa control. Most of the samples which reduced algal growth were collected from the Feather and American rivers and from the Sacramento River upstream of Redding. Unlike the results obtained with fathead minnows and *C. dubia*, there did not appear to be a seasonal component to the algal responses. Nearly 20 percent of the samples tested produced toxicity to this species.
- The results suggested that presence of toxicants in the upper part of the Sacramento

River, particularly copper, zinc, nickel, and cadmium, decreased as the River approached Colusa. Downstream of Colusa, adverse effects appeared to be predominantly associated with agricultural discharges, especially during the rice discharge season.

- Samples from the Feather River generally did not affect the fish but affected *C. dubia* approximately 50 percent of the time. Most of the toxic samples appeared to be associated with rice discharges. *S. capricornutum* were also affected by an appreciable portion of samples collected from the Feather river. There did not appear to be a seasonal component to the toxicity.
- Adverse effects on fathead minnows were shown in the American River, particularly related to storm events. The survival of *C. dubia* was reduced in over half of the samples collected from the American River. Storm events appeared to have a role in toxicity, and the frequency of toxic events increased as samples were collected further downstream of Nimbus Dam. The algal response was similar to that observed with *C. dubia*. The authors proposed that metals could be a cause of toxicity in this watershed.
- Sampling was more limited in the Delta sites, but all three species responded to samples collected from the Delta. *C. dubia* responded most frequently, and the seasonal pattern of responses suggested that toxicity was attributable to rice discharges, as well as local sources.
- Compared with the San Joaquin drainage, the Sacramento River had proportionately more toxic samples from the main river bodies with respect to the fathead minnow test. The results for *C. dubia* were qualitatively similar in both watersheds; toxicity was distributed across the main rivers and agricultural drains and was frequently attributed to pesticides. The algae appeared to grow better in water from the San Joaquin drainage than from the Sacramento drainage.

Herbold *et al.* (1992) prepared a report on the status and trends of aquatic resources in the San Francisco Estuary. In general, the report emphasized relationships with water flows and exports, although possible effects of toxic contaminants were also noted. These authors grouped factors which controlled the distribution and abundance of organisms in the Bay and Delta into three categories. The first was climate, with variation in ocean conditions (El Nino events), rain, and snowfall predominating. The second was the physical features of the

estuary, including basin morphology, salinity, and temperature. Human activities comprised the third category which included introduced species, pollution, modification of waterways and wetlands, and alterations of patterns of freshwater inflows and outflows. A general description of their findings follows:

- Recent changes in primary producers include blooms of *Melosira*, a diatom that is difficult for most zooplankton grazers to feed upon, and a reduction of phytoplankton in Suisun Bay. The latter is apparently a result of extensive filter feeding by the recently introduced clam *Potamocorbula amurensis*.
- Populations of the smallest zooplanktons, rotifers, have declined dramatically since the mid-1970s, especially in the Delta, and are currently at very low levels. Cladocerans have also declined markedly since the mid-70s. Most of the freshwater copepods have shown declines similar to those of the cladocerans, while marine species do not demonstrate such trends. The estuarine copepod *Eurytemora affinis* has also shown a marked decline in numbers. *Neomysis* abundance is tied to the abundance of *Eurytemora* and to freshwater flows. All of these organisms are extremely important to obligate planktivorous fishes as well as larval and juvenile life stages that are also obligate planktivores.
- Historically, the distribution and abundance of benthic species has been dominated by changes in salinity that result from the interplay between freshwater outflows and saltwater intrusion. Both Dungeness crab and grass shrimp *Crangon franciscorum* appear to show long-term declines in abundance. The crab population may be more related to marine conditions while the shrimp population may be tied to freshwater outflow.
- Chinook salmon and other salmonids have undergone major declines in population. While this has been largely due to factors and events that have occurred upstream of the Delta, recent evidence suggests that high mortality of out-migrating smolts may occur under conditions of low Delta outflow and high export pumping rates.
- Striped bass have also undergone a major reduction in numbers since the mid-1970s. Factors contributing to the decline include toxic contaminants, reduced food supplies, reduced egg production, overfishing, and, according to the authors, the overwhelming effect of water diversions.
- White sturgeon are also declining. The major effects seem to be the harvest rate and its

spawning success being tied to very high outflows.

- Planktivorous marine fish species, such as herring and anchovy, generally show no long-term trends. Conversely, estuarine and freshwater planktivores, including threadfin shad, and Delta and longfin smelt, have shown long term declines in numbers.
- White croaker, a predominantly marine species, has increased in abundance.
- English sole, a predominantly marine flatfish, has shown no decline in numbers. However, the estuarine starry flounder has shown a decline in numbers which may be related to hydrologic conditions in San Pablo and Suisun Bays and also to levels of toxic contaminants.
- Two other estuarine or freshwater species, the white catfish and Sacramento splittail, are also showing long term declines in abundance. Conversely, the introduced chameleon goby is expanding its range through the upper part of the estuary.
- An analysis of changes in sources and loadings of organic carbon suggests that declines in organic carbon loading to the upper estuary since the early 1980s probably resulted in a decline in fish production over that same period.
- Both dead-end sloughs and smaller tributaries to the estuary were noted as very important habitats for a variety of life history stages and endemic species.

A report on the status and trends of wildlife associated with the San Francisco Estuary was prepared by the U.S. Fish and Wildlife Service (Harvey *et al.* 1992). The report divided the Estuary into different habitat types and the communities they support. Most of the habitats and associated organisms have been heavily impacted by detrimental anthropogenic activities including over-harvesting, conversion of native habitats to agricultural and urban uses, alteration of water flow patterns, and the introduction of non-native species. Consequently, most of the habitats have been dramatically reduced in size, and much of what remains is fragmented, further increasing the vulnerability of resident organisms. Additional findings include:

- Wetland and riparian habitats are the two rarest native habitats in the Estuary.
- Introduction of chlorinated hydrocarbon pesticides in the 1940s eliminated bald eagles, osprey, peregrine falcons, and brown pelicans from the Estuary. These populations recovered to some extent once DDT was banned.

- Oil spills and gill nets have killed large numbers of aquatic birds that use the Estuary. Aquatic mammals have also been adversely affected by oil spills in the Estuary.
- Reproductive success of night herons may be adversely affected at some sites in the Estuary; both abnormal embryos and crushed eggshells have been found in rookeries (Bair Island), and DDE concentrations in night heron and snowy egret eggs exceeded the threshold for reproductive impairment (Bair and West Marin Islands). PCB residues in night heron embryos were negatively correlated with weight. DDE and PCB concentrations in night-heron and snowy egret chicks increased as the chicks grew, indicating a local source for the contaminants.
- Concentrations of PCBs in Caspian terns were higher in San Francisco Bay than in San Diego Bay or Elkhorn Slough.
- In general, evidence is accumulating that PCBs are having detrimental effects on local biota.
- Levels of mercury in clapper rail eggs are at levels that have caused embryotoxicity in mallards. Selenium concentrations were high in clapper rail eggs collected near an oil refinery in North Bay.
- Levels of DDE, PCBs, metals, and selenium in blood samples from harbor seals from San Francisco Bay were much higher than levels from seals from Puget Sound. PCB concentrations in the seals are similar to those that have caused reproductive problems in seals elsewhere.
- Monitoring of sediments, algae and invertebrates at sites in San Francisco and San Pablo Bays indicated toxic concentrations of mercury, selenium, cadmium, aluminum, lead, chromium, copper, and zinc were present at one or more sites. This has negative implications for waterfowl which feed on contaminated organisms and for organisms that inhabit contaminated areas.
- Diving ducks that feed on benthic invertebrates such as mussels and clams have been shown to contain high levels of mercury, cadmium, selenium, copper, lead, iron and zinc. Selenium levels, which were highest in birds sampled from San Pablo and South Bay, were at concentrations that caused adult mortality and reproductive impairment at Kesterson Reservoir. Mercury concentrations exceeded those that caused behavioral and reproductive effects in mallards. A human health advisory has been issued regarding the selenium levels in two species of diving ducks.

- Sources of trace elements include sewage treatment plants. Primary sources of selenium are sewage treatment plants in the South Bay and oil refineries in the North Bay. PCBs are widespread throughout the Bay, with local "hot spots" such as Richmond and Oakland Harbors. Locally, the Richmond Harbor area is heavily contaminated with chlorinated hydrocarbon pesticides, but some of these chemicals continue to enter the Estuary as soils are eroded and exported from the Central Valley.
- Freshwater inflows are critical for the flushing of contaminants from the system.
- It is likely that the effects of contaminants will increase as the population of the area increases, placing an even greater burden on the POTWs and industrial and stormwater treatment systems.
- The effects of arsenic and tin have not been well-studied; these materials occur locally at high concentrations.
- Predation by introduced species on nesting birds, eggs and offspring is a significant problem in many of the colonial nesting areas. This problem is exacerbated by the relatively low number of such sites.
- Powerlines and wind farms in the area are a continual source of mortality for raptors and other birds.
- Reptilian and amphibian populations have been severely reduced throughout the Estuary.

The San Francisco Regional Water Quality Control Board, in conjunction with the State Water Resources Control Board and California's Department of Fish and Game, conducted a pilot study to evaluate the levels of contaminants in fish collected from San Francisco Bay (SFRWQCB 1994). The primary concern of the study was to identify tissue levels that might pose a threat to human health. Fish were collected from 13 stations around the Bay. Species sampled included white croaker, striped bass, sturgeon, shiner surfperch, walleye surfperch, halibut, brown smoothhound sharks, and leopard sharks. A total of 66 composite edible tissue samples were analyzed for trace metals, PAHs, PCB congeners, and pesticides. The major findings included:

- Tissue concentrations of PCBs, mercury, dieldrin, total chlordanes, total DDTs, and total dioxin/furans exceeded EPA screening guidelines in at least some of the composites.
- In spite of long-term monitoring data in mussels that suggest that PCB concentrations in the Bay have declined since 1979, PCB levels in all of the tissue composites exceeded

the EPA screening value of 3 ppb. White croaker at some locations achieved concentrations of 638 ppb.

- Mercury concentrations exceeded the screening value of 0.14 ppm in approximately 2/3 of the samples. The highest levels, up to 1.26 ppm, were found in sharks.
- Slightly over 50 percent of the composite samples exceeded the screening value for dieldrin (1.5 ppb). White croaker, striped bass, and shiner surfperch were the primary species affected.
- Total chlordane concentrations in tissue samples exceeded the screening value of 18 ppb in approximately 10 percent of the samples. The highest concentrations were found in the vicinity of Mare Island-Vallejo in white croaker (36 ppb).
- Total DDTs exceeded the screening value of 69 ppb in approximately 14 percent of the samples. The highest concentrations (155 ppb) were found in white croaker from the north end of the Bay. Mussel watch data suggests that DDT concentrations in the Bay have been declining since the mid-1970s.
- Only 19 composites were analyzed for dioxin equivalents. Sixteen of these samples exceeded the screening value of 0.15 ppt. The highest values were found in white croaker from the South Bay.
- PAH concentrations were consistently near or below method detection levels in all samples.

The first annual report of the San Francisco Estuary Regional Monitoring Program described the results of studies conducted in 1993 (SFEP 1993). Measurements of trace contaminants and water quality were obtained from 16 stations 2 or 3 times during the year. Sediment and water column toxicity tests were conducted at 8 stations and bioaccumulation in bivalves was determined at 11 stations. Major findings included:

- Cadmium, arsenic, zinc, copper, nickel, silver, and selenium concentrations were generally highest in the South Bay, followed by the North Bay (the highest copper concentration was obtained from Grizzly Bay). Mercury and nickel were high in San Pablo and Suisun Bays, and chromium and lead were highest at stations near the confluence of the Sacramento and San Joaquin rivers. Most of the metals reached their highest concentrations during periods of high run-off. A comparison with monitoring

data back to the 1970s suggests that the concentration ranges are similar. The concentrations of metals exceeded water quality objectives at six stations.

- Sources of metals included rivers and local runoff, as well as point sources.
- PCBs were high in the South Bay and in the Napa River. PAHs were high in both the South and Central Bays and pesticides were highest in the Sacramento River and the lower South Bay. PCB concentrations exceeded human health objectives at all stations. Chlordane, dieldrin and DDTs exceeded EPA objectives at several stations, including the Sacramento River, Napa River, and Grizzly Bay. A comparison of PCB concentrations with those obtained from the 1970's suggests concentrations may be declining overall, although additional data will be required to establish a trend.
- Water column toxicity tests with algae and bivalve larvae generally did not indicate toxicity, but the low number of sampling events and high variability (between replicates in toxicity tests and in reference toxicant tests conducted for quality assurance) precluded definitive conclusions.
- Sediment PCBs and PAHs were highest in the Central Bay; pesticides were highest in the North Bays and lower South Bay.
- Nickel was the only trace contaminant in sediment that exceeded NOAA's Median Effects Ranges; it was high at all stations.
- Sediment toxicity tests with amphipods and bivalve larvae indicated toxicity at all stations.
- Transplanted bivalves accumulated metals, PCBs, PAHs, and pesticides, sometimes to a large degree. Large seasonal differences in accumulation were noted, particularly with respect to some of the metals. Pesticides were accumulated to the greatest degree in Grizzly Bay and River stations. Poor survival was noted in bivalves held in the Napa River.

Most recently, the San Francisco Estuary Project produced a Comprehensive Conservation and Management Plan for the Bay – Delta Region (SFEP 1993). The Plan noted that the reduction of conventional pollutants since the 1950s has largely eliminated odor problems, algal blooms, and low dissolved oxygen levels. However, concern remains that trace inorganic and organic substances still occur at concentrations that adversely affect aquatic life. These materials include some metals, pesticides, and petrochemical hydrocarbons. The Plan estimated that

between 5 and 40,000 tons of some 65 different contaminants enter the Estuary annually from point and non-point sources, atmospheric deposition, spills and dredging. These contaminants include copper, zinc, nickel, silver, pesticides, PCBs, and PAHs. Deleterious effects on starry flounder and black-crowned night herons were noted. In addition, with expected increases in urban land uses, pollutant loadings are expected to increase commensurately unless steps are taken. To address this issue, the Plan describes a recommended approach, goals and actions that need to be implemented to effectively reduce concentrations of toxic contaminants in Bay-Delta waters.

One of the components of the Plan calls for the identification and control of contaminants that may affect fish populations or ecosystem health (SFEP 1993). This effort is to be implemented as quickly as feasible, with the year 2030 as the goal for reducing all toxicants to levels that cause no adverse effects. [The utility of a timeframe that extends so far into the future is questionable; it may simply mean that the deadline is far enough into the future so as not to be threatening to current user groups and resource managers. More to the point, delaying action on toxic contaminants will only reduce the benefits of other efforts to improve the health of the system and, in fact, may obscure the benefits of these actions, such as altered flows and exports and screening of diversions, which are currently being taken to help restore populations of Bay/Delta organisms.]

As part of the effort to address toxic contaminants, the Plan provides the following recommendations regarding pesticides (SFEP 1993):

- Pesticide registrants should provide data to Department of Pesticide Regulation and Regional Water Quality Control Boards which demonstrate the proposed use will not result in surface water concentrations that exceed Basin Plan objectives. [This recommendation should apply to products currently in use as well as new products.]
- Water Quality Control Plans should contain numerical objectives for all pesticides detected in the Estuary.
- Best Management Plans should be implemented immediately for agricultural use of pesticides. If the BMPs do not reduce concentrations to acceptable levels, consider implementation of waste discharge requirements.
- The State and Regional Boards should develop an enforceable instream toxicity program,

which would include toxicity and analytical monitoring, assessment of compliance with objectives, detection of new problems, and the success of control measures.

Compliance points should be selected for measuring chronic toxicity.

- Analytical methods should be capable of detection levels that are less than concentrations that produce adverse effects.

The Plan also addressed funding strategies, enforcement, control of aerial drift from pesticide application, and provided a framework for cooperation between pesticide manufacturers and regulatory agencies.

Urban run-off was also addressed in the Plan (SFEP 1993). The proposed program focused on prevention upon identification of problematic contaminants. The Plan suggested that Regional Boards consider enforcement activity against municipalities that fail to control toxic contaminants in urban watersheds.

The Plan pointed out that trace metal contaminants from inactive mining sites should also be addressed (SFEP 1993) by identification of problem sites, followed by control measures to reduce discharge of metals. Proposed sources of funding included a combination of state Clean-up and Abatement funds and responsible parties.

The importance of these efforts to the health of the Estuary was demonstrated by the final recommendations for pollution prevention and reduction (SFEP 1993). These recommendations, aimed at toxicants present in the water column and sediments, called for the Resource Agencies to identify and reduce contaminants presently affecting fish, wildlife, their habitats and food supplies. Furthermore, it was recommended that Resource Agencies should immediately seek damages from the responsible parties to provide a funding basis for the clean up or remediation of contaminants adversely affecting public trust resources.

FINDINGS

AMBIENT TOXICITY

Sacramento and San Joaquin Rivers

Comparatively few studies have investigated toxicity in ambient waters in the Bay/Delta system. However, the Central Valley Regional Water Quality Control Board has maintained a program investigating toxicity in ambient waters of the Region with the standard USEPA 3-species test for nearly ten years.¹ In 1986, toxicity was noted in the Sacramento River at Sacramento using *Ceriodaphnia dubia* as the test organism (Foe and Connor 1991). In 1987, follow-up work suggested that much of the toxicity was related to seasonal discharges associated with rice culture and toxicity was found in the Sacramento River approximately 2 miles downstream of Colusa Basin Drain, which enters the River at Knight's Landing. Elevated mortality was also seen with fathead minnows exposed to water collected at this site. Similar results were obtained in 1988. However, toxicity was found both above and below Colusa Basin Drain which made it difficult to separate the sources of toxicity. In 1989, monitoring with *C. dubia* at the end of May showed elevated mortalities at all sites on the river down to Rio Vista, 75 miles downstream of Colusa Basin Drain (this was the lower-most sampling site; toxicity may have extended even further downstream). One week later, elevated mortalities appeared to be limited to the stretch 30 miles downstream of the Drain (Foe and Connor 1991). Follow-up Toxicity Identification Evaluations (TIEs) conducted by EPA indicated that carbofuran and methyl parathion, two pesticides applied to rice, were responsible for toxicity to *C. dubia* in 1988 (Norberg-King *et al.* 1991). TIEs conducted on samples collected from CBD in 1989 suggested that carbofuran and methyl parathion were responsible for toxicity to *C. dubia* (Norberg-King *et al.* 1989).

Bailey reported reduced survival of striped bass larvae exposed to one sample collected from the Sacramento River at Rio Vista on 15 May 1988 (Appendix B in Foe and Connor 1991). In

¹Test species include *Ceriodaphnia dubia* (invertebrate), *Pimephales promelas* (fish), and *Selenastrum capricornutum* (alga). See EPA (1991b) for test procedures.

1989, two samples collected from the Sacramento River at Walnut Grove produced nearly complete mortality of larval striped bass within 96 hours. These samples were collected at the end of May and early June during the rice discharge season.

Finlayson *et al.* (1993) reported on the toxicity of samples collected from the Sacramento River at Rio Vista during rice season 1990. Three of the 30 samples significantly ($p < 0.05$) reduced the survival of *N. mercedis* within 96 hours. These samples were also tested with striped bass larvae, but high and variable control mortalities made it problematic to assess the extent of toxicity to this species. The authors noted that the cause of the striped bass decline could be direct effects on striped bass and/or to their food organisms.

Samples were collected in the Sacramento River at Garcia Bend between December 1990 and November 1991 and tested for toxicity with *C. dubia* and fathead minnows (AQUA-Science 1993). Of the nine samples collected, 6 significantly increased mortality in the fathead minnows tested. No adverse effects were noted with *C. dubia*. Between February 1992 and November 1992, the sampling site was changed to Freeport. Of 6 samples tested with fathead minnows, one produced elevated mortality and another reduced growth. Two of the samples also reduced the survival or reproduction of *C. dubia*. Three additional collections were made at Freeport between November 1993 and March 1994 and ambient toxicity evaluated with the 7-day fathead minnow test (AQUA-Science 1993 and 1994). No toxicity was observed in the sample collected in November, but survival and growth were adversely affected in the sample collected in February 1994. A follow-up sample collected in March also exhibited reduced survival.

Toxicity was also monitored during four rainfall periods during winter 1993 – 1994 (Bailey *et al.* in prep). In the first period, 6-hour composite samples were collected over a two-day period at Green's Landing on the Sacramento River. One of the six samples collected exhibited toxicity to all three of the test species, including increased mortality in *C. dubia* and fathead minnows.

In the second period, samples were collected daily between 23 and 28 January. Complete mortality was seen with *C. dubia* exposed to samples collected from the San Joaquin River at Vernalis from 24 through 27 January. A follow-up TIE suggested that the mortalities were due

to metabolically activated organophosphorous pesticides. One sample collected at Vernalis also reduced algal growth to approximately half of that seen on the four previous sampling days. No adverse effects were observed with *C. dubia* or the alga exposed to samples collected from the Sacramento River at Green's Landing during this same sampling event. However, growth was significantly reduced in fathead minnow larvae exposed to samples collected at Green's Landing 24 and 25 January.

A third series of tests evaluated toxicity at the same sites during another precipitation event (6-13 February 1994). Toxicity to *C. dubia* was apparent in samples collected 8-11 February at Vernalis. None of the samples collected at Vernalis exhibited toxicity to fathead minnows, but the sample collected 9 February reduced algal cell numbers. One sample collected from the Sacramento River (11 February) exhibited toxicity to *C. dubia* and one sample also exhibited toxicity to fathead minnows (10 February). None of the samples collected from the Sacramento River exhibited toxicity to the alga.

Additional samples were collected from the San Joaquin River at Vernalis between 17 and 23 February 1994. None of these exhibited toxicity to any of the three test species.

In January 1995, daily samples were collected from Sacramento River at Greene's Landing and the San Joaquin River at Vernalis over a precipitation event lasting between 9 and 14 January (Deanovic *et al.* in prep). Reproduction in *C. dubia* was significantly reduced in all five of the samples collected from the Sacramento River and in 2 of the 6 samples collected from the San Joaquin River. There were no adverse effects noted with fathead minnows. There were no adverse effects noted with *S. capricornutum* exposed to the Sacramento River samples, but a generally increasing trend in cell numbers in the San Joaquin River samples collected over time suggests that cell numbers were limited by water quality at the beginning of the rain event.

Delta

In late winter 1991-1992, eleven sites on tributaries to San Francisco Bay/Delta were monitored for toxicity associated with orchard run-off (Foe and Shepline 1993). The sites were divided between the Sacramento and San Joaquin Basins. Six sites represented

watersheds that ranged between 10,000 and 130,000 acres, with at least 10 percent of this total in orchards. The remaining five sites represented larger water bodies, including the Sacramento River, Feather River, Mokelumne River, Old River, and the San Joaquin River. Intermittent toxicity was observed in the smaller drainages during dry weather. However, all of these drainages exhibited toxicity during the period of precipitation that occurred between 4 and 20 February 1992. Of the larger water bodies, only the Mokelumne River exhibited toxicity during the dry period. However, once runoff occurred, samples from the Feather, Old and San Joaquin Rivers also exhibited toxicity. Toxicity persisted in the San Joaquin River for some time following the storm. A total of 25 samples exhibited toxicity, and in 22 cases, the organophosphorous pesticides diazinon and/or methidathion were present at concentrations high enough to produce acute mortality. Concurrent chemical monitoring data suggested that the San Joaquin River was acutely toxic for at least 8 days (12-19 February) and that this water reached as far north as Empire Tract and Venice Island before being diluted by flows from the Sacramento and Mokelumne Rivers. These investigators concluded that the toxicity was largely due to the presence of pre-emergent pesticides, primarily diazinon, that had been applied to the orchards and were transported off-site in run-off from rain.

Toxicity associated with run-off from sites in the Delta that grew alfalfa was evaluated during March and April 1992 (Foe and Shepline 1993). Intermittent toxicity was observed, particularly in Ulatis Creek, Bishop Tract Main Drain, and Paradise Cut. Analytical results indicated that both carbofuran and diazinon were present at potentially lethal concentrations in some of the samples. The authors felt that the data were representative of a "dry year" because no precipitation related run-off occurred during the study period.

Toxicity in samples collected primarily from Hog, Sycamore, and Beaver Sloughs was evaluated with *C. dubia* in May and June 1994 (DiGiorgio *et al.* 1994). Samples were collected weekly from different sites, but only one of the 60 samples collected exhibited toxicity to *C. dubia*. This may have been a consequence of the time of sample collection; very little pesticide applications were occurring in these watersheds during the study period and no rainfall events occurred.

Delta sites were monitored twice monthly between May 1993 and May 1994, alternating

between sites on the Sacramento and San Joaquin sides, using short-term chronic tests with fathead minnows, *C. dubia*, and *Selenastrum capricornutum* (Deanovic *et al.* in prep.). Sampling sites included major rivers and channels, back sloughs, and island drains (see Appendix A for sampling sites). The results, based on a preliminary analysis of the data, are summarized below:

<u>Sacramento side</u>	<u>MAY</u>	<u>JUN</u>	<u>JUL</u>	<u>AUG</u>	<u>SEP</u>	<u>OCT</u>	<u>NOV</u>	<u>DEC</u>	<u>JAN</u>	<u>FEB</u>	<u>MAR</u>	<u>APR</u>	<u>MAY</u>
No. tested	15	11	12	15	12	12	--	12	--	--	13	12	12
No. toxic	7	5	6	7	8	4	--	8	--	--	4	1	4
<u>San Joaquin side</u>													
No. tested	12	12	12	12	12	12	12	--	12	--	--	12	13
No. toxic	5	9	5	3	1	5	2	--	0	--	--	3	4

During most of the year, adverse effects were observed in approximately 33 to 75 percent of the samples with one, or more, of the test species. Months in which ≤ 10 percent of the samples toxic were April (Sacramento River side of the Delta) and September and January (San Joaquin side of the Delta). In most cases, toxicity was associated with the smaller creeks and sloughs and the island drains. However, larger waterways were also frequently affected. In ten testing events conducted between May 1993 and May 1994 on each side of the Delta, toxicity was found in samples collected in the Sacramento River (6 events), San Joaquin River (3 events at Vernalis and 5 events at Antioch), Old River (7 events), Middle River (1 event), and the Mokelumne River (5 events). The Port of Stockton site, which was considered to be dominated by urban inputs, exhibited toxicity in 4 events. Samples collected from the Delta-Mendota Canal also exhibited toxicity in 4 sampling events. These numbers would appear to be of concern; not only were the smaller creeks and sloughs affected, but also large masses of water moving through the Delta appeared to be contaminated as well.

Species sensitivity varied. In most cases, only one of the test species responded to a particular sample, implying that different toxicants were responsible. Based on the preliminary analysis, a total of 42 samples exhibited toxicity to *C. dubia*, 36 samples were toxic to fathead minnows, and 28 samples were toxic to *S. capricornutum*. Only 7 samples exhibited toxicity to both fathead minnows and *C. dubia*, and 6 samples exhibited toxicity to *C. dubia* and *S. capricornutum*. None of the samples exhibited toxicity to both the alga and fathead minnows.

More recent sampling was conducted on Delta sites between 1 December 1994 and 28 February 1995 (Deanovic *et al.* in prep). In December, samples from 9 sites were tested with *S. capricornutum*. Algae exposed to samples from two of these sites, Rock and Prospect Sloughs, exhibited reduced cell numbers. Samples from 16 sites were tested with *C. dubia*. Samples from three of these sites, Ulatis Creek., Haas Slough., and Mosher Slough., produced complete mortality. In all three cases, TIEs identified organophosphorous pesticides as the cause of toxicity. Five samples were tested with fathead minnows; none exhibited adverse effects on growth or survival.

In January 1995, samples collected from 12 sites were tested with *S. capricornutum*. Four of the sites, Haas Slough., Duck Slough., Victoria Island Drain, and Old River exhibited one third to one half of the growth apparent in samples from the other sites (Deanovic *et al.* in prep). All of these samples, with the exception of Haas Slough., were passed through C8 SPE columns which selectively remove non-polar organic chemicals and re-tested. In all cases, cell numbers increased by 4- to 5-fold over the untreated samples, suggesting that non-polar organic chemicals were responsible for toxicity. Eleven sites were tested for toxicity with *C. dubia*. Complete mortality occurred in the sample from Mosher Slough. and reduced reproduction occurred in samples from six of the remaining sites. These sites were Ulatis Creek., Haas Slough., Ryer Island Main Drain, Duck Slough., Pierson Tract, Victoria Island Drain, and Middle Roberts Island Drain. The toxicity in Mosher Slough. was due to an organophosphorous pesticide; both diazinon and chlorpyrifos were present in the sample at concentrations sufficient to cause acute toxicity.

San Francisco Bay

As part of an Effluent Characterization Program that was initiated by the Regional Water Quality Control Board involving San Francisco Bay dischargers, ambient water samples collected from different sites in the Bay were also monitored for toxicity on a monthly basis (see summary table in Appendix B). The test species were selected on the basis of a preliminary screening study and varied with site. The data from ten dischargers with available records are summarized below:

	<u>Percentage of Samples Exhibiting Toxicity</u>				
	<u>< 20%</u>	<u>≥ 20%</u>	<u>≥ 30%</u>	<u>≥ 40%</u>	<u>≥ 60%</u>
No. of Sites (n = 10)	3	7	7	6	3

Only three of the sites exhibited toxicity less than 20 percent of the time, while the remaining sites exhibited toxicity at least 30 percent of the time. Six sites exhibited toxicity at least 40 percent of the time and half of these exhibited toxicity over 60 percent of the time. Sites exhibiting toxicity at least 40 percent of the time included New York Slough, Suisun Bay, South Bay, and the Napa River. Species exhibiting adverse effects included silversides, echinoderms, *C. dubia*, diatoms, abalone, and bivalves.

Anderson *et al.* 1990 conducted ambient toxicity tests on samples collected quarterly from 12 sites in San Francisco Bay. Test protocols used included the echinoderm fertilization bioassay, the *Menidia* 7-day larval survival and growth test, the 4-day diatom (*Skeletonema*) growth test, and the mollusc embryo development test. In the first testing event (April 1989), *Skeletonema* and the echinoderm tests exhibited the greatest responses. Echinoderm fertilization success was reduced to less than 30 percent at all sites, compared with 98 to 100 percent in the controls. Growth of *Skeletonema* was reduced by at least 40 percent in samples from 7 sites, including nearly all of the sites located in South and Central Bays. There did not appear to be any adverse effects on survival or growth of *Menidia*. Survival of mussel larvae appeared reduced in a sample from only one station located in the South Bay.

Skeletonema were not used in the remaining three testing events. In the August 1989 sampling event, echinoderm fertilization was reduced at only one Central Bay site and again at all of the South Bay sites. The survival of oyster larvae appeared reduced at one Central Bay site and two South Bay sites. There did not appear to be any adverse effects on *Menidia* larvae at any of the sites.

Samples collected during December 1989 reduced echinoderm fertilization success in samples from 9 sites, distributed equally across North, Central, and South Bays. The survival of mussel larvae appeared reduced at 3 sites in Central Bay and one site in South Bay. Again,

there were no adverse effects on *Menidia* larvae.

Only echinoderms were tested during April 1990. Reduced fertilization success was noted in samples from three of the four South Bay stations, two of the four Central Bay stations, and all four of the North Bay stations. Fertilization success averaged approximately 90 percent in the controls compared with 29 to 65 percent in the Bay samples.

Water samples were also collected from several Bay marshes used for reclamation projects or adjacent to discharge sites (Anderson *et al.* 1990). Three sites from the San Francisco Bay National Wildlife Refuge were tested with the echinoderm fertilization test, the *Menidia* larval test and *Skeletonema*. Fertilization success was reduced at one site; there were no other adverse effects found.

Samples from 6 sites in the Hayward Marsh Reclamation project, which receives water from the Union Sanitary District, were tested with *Menidia* and echinoderms (July 1989). Toxicity to both species was found at the three of the four upstream sites, but not at the two lower stations. This survey was repeated in November with similar results. Anderson *et al.* (1990) suggested that ammonia was a major source of toxicity at this site.

Samples collected from the Mountain View Sanitary District Marsh and Peyton Slough, also exhibited toxicity. Algal growth was inhibited in all five of the samples tested, echinoderm fertilization was dramatically reduced in three of the nine samples tested, and fathead minnow growth and survival were reduced in one of the nine samples tested. Interestingly, there were no effects on *Ceriodaphnia* in any of the nine samples tested.

Samples collected from Sunnyvale Marsh, which receives water from the Sunnyvale sewage treatment plant, exhibited toxicity to *Selenastrum*, *Ceriodaphnia*, and echinoderms. No adverse effects were found for fathead minnows exposed to samples collected from any of the nine sites associated with this marsh.

The San Jose/Santa Clara Marsh also receives freshwater from a POTW. No toxicity was found at any of the 10 sites associated with this Marsh using the 7-day *Menidia* and mysid tests and the echinoderm fertilization test (Anderson *et al.* 1990).

Anderson *et al.* (1990) also reported on toxicity studies conducted with samples collected during a dredging operation at Oakland Harbor. *Skeletonema* was the only species that exhibited an adverse response where growth was reduced in samples from three of the five stations. There were no effects noted with either *Menidia* or mollusc larvae.

Anderson *et al.* (1990) also found toxicity associated with the Contra Costa Canal using echinoderms and *Ceriodaphnia*. *Menidia*, mollusc larvae and *Selenastrum* were not affected. This canal originates at Rock Slough in the Delta.

Additional Studies in the Watershed

Some studies conducted on portions of the Sacramento-San Joaquin watersheds fell outside the review boundaries. However, the results may be of interest with respect to impacts on local organisms. In addition, some of these areas serve as spawning and nursery habitat for migratory species that utilize the Estuary. Adverse effects on invertebrates and algae in these upstream areas could reduce forage and also reduce the abundance of zooplankton and algae transported downstream to the Estuary. These studies are briefly summarized below:

Between 1988 and 1990, samples were regularly collected from the San Joaquin drainage and tested for toxicity with the EPA three-species test (Foe and Connor 1991). A 43-mile section of the San Joaquin River located between the Merced and Stanislaus Rivers exhibited toxicity to *Ceriodaphnia dubia* about half of the time, primarily due to pesticides in run-off from row and orchard crops. Although this stretch of the San Joaquin River is upstream of the Delta, reduced invertebrate populations in the River could reduce invertebrates exported to the Delta and indirectly impact Delta fish species that rely on this portion of the river for part of their life cycle. Of note, all of the salmon stocks associated with the San Joaquin drainage have declined drastically due to a number of reasons (Reynolds *et al.* 1993) and reduced forage could certainly impact the growth and survival of the juveniles.

Water samples collected from the Cache Creek drainage in winter 1994-1995 revealed high mercury concentrations, up to 2 µg/L. In dry years, flows from Cache Creek terminate in the

Yolo Bypass. However, in wet years, high flows through the Bypass will transport Cache Creek waters into the Delta. The data suggest that large quantities of mercury could be exported to the Delta from this watershed, especially during high flow years. Some of the samples collected from this drainage during high flow periods were also tested for toxicity with *C. dubia* and *S. capricornutum* (Foe *et al.* unpublished). Nine samples collected from this drainage between 9 and 21 March 1995 produced between 33 and 100 percent mortality (median = 80 percent) in *C. dubia* within 8 days, compared to control mortality of 3.3 percent. A sample collected from Cache Creek on 2 May 1995 reduced reproductive output in *C. dubia* by 20 percent, compared with the control. Two samples were tested with *S. capricornutum*, and neither resulted in decreased cell numbers. Due to limited sample volumes, no Toxicity Identification Evaluations were performed on these samples to determine the cause of toxicity.

Clearly, toxicity occurs on a frequent basis in water samples collected from the Estuary and its tributaries. In some cases, toxicity appears to be associated with rainfall events, while in other cases, toxicity can be related to local inputs. Toxicity may also be related to specific cropping practices, such as rice production, although recent data suggest that more restrictive pesticide use requirements have reduced toxicity associated with this particular crop (Bailey *et al.* 1994b). In any case, the frequency of toxicity suggests that USEPA's guidance for maintaining water quality is being exceeded in the Delta much more frequently than the one event per three-year interval estimated to be necessary to allow for recovery of an impacted system.

SOURCES OF TOXICITY

Agricultural Inputs

Determination of adverse effects associated with agricultural inputs into Estuary waters has been largely ignored until fairly recently. This has been reflected by a general lack of analytical monitoring for associated pesticides in Bay and Delta waters, as well as in lack of toxicity testing of these waters. Agricultural inputs may be transported into the Estuary from upstream drainage basins (e.g., the Sacramento, Feather, and San Joaquin Basins, for example) or they may arise as direct inputs from agricultural practices in the Delta itself. According to the

Department of Water Resources (1987), there are over 200 agricultural return drains operating in the Delta. Agricultural inputs may include suspended sediment, various fertilizers, and pesticides. High concentrations of ammonia may be associated with discharges from dairies and feedlots. However, in general, pesticides appear to be the major source of toxicity in agricultural waters discharged to the waters that enter the Delta.

As a result of studies that suggested that pesticides were adversely affecting water quality in the Estuary and its tributaries (see, for example, Bailey *et al.* 1994; Finlayson *et al.* 1993; Foe and Sheipline 1993; Foe and Connor 1991; Norberg-King *et al.* 1991; Foe and Connor 1989), California's Department of Fish & Game initiated the process of producing water quality criteria for pesticides of interest. Criteria have been developed for molinate and thiobencarb (Harrington 1990), carbofuran (Menconi and Gray 1992), methyl parathion (Menconi and Harrington 1992b), and chlorpyrifos (Menconi and Paul 1994). A draft document for diazinon has also been completed (Menconi and Cox 1994). Values of 0.5 and 0.08 µg/L were recommended for carbofuran and methyl parathion, respectively, to protect aquatic life. An interim value of 0.02 µg/L was recommended for chlorpyrifos, and diazinon concentrations protective of acute and chronic toxicity were 0.08 and 0.04 µg/L, respectively.

Rice culture constitutes the single largest use of irrigation water in the Sacramento Valley. Rice return flows, which can comprise up to 33% of Sacramento River flow, are discharged along a 90 km stretch of river between Colusa and Verona at the mouth of the Feather River (Cornacchia *et al.* 1984). Significant inputs to the River include Colusa Basin Drain, Butte Slough, and Sacramento Slough. Input from Colusa Basin Drain alone can account for approximately 25 percent of the flow of the Sacramento River in some years. Most of the discharge enters the Sacramento River upstream of Sacramento. However, in years of high river flow, discharge from Colusa Basin Drain may be diverted into the Yolo Bypass and enter the Sacramento River via Prospect Slough, downstream of Sacramento. Because of the comparatively large contribution of rice return flows to the overall flow of the Sacramento River, the capacity for dilution of incoming toxicants is relatively low once they reach the River.

Monitoring of the Delta for the rice herbicides molinate and thiobencarb was not initiated until 1985, even though large fish kills associated with agricultural drainage from rice culture had

been observed several years earlier (SWRCB 1990). Measured concentrations of molinate and thiobencarb in 1985 suggested that concentrations toxic to *Neomysis mercedis* were approached in the upper Delta (Bailey 1993). In subsequent years, more restrictive pesticide management practices (increased on-field holding times) reduced concentrations of these pesticides in the Delta to levels below those associated with toxicity, although molinate and thiobencarb have been detected in the Delta as recently as 1993 (K. Kuivila, USGS, personal communication). In the years between 1982 and 1985, extrapolation from measured concentrations in Colusa Basin Drain suggests that the toxic threshold for *N. mercedis* for these pesticides could have been exceeded by a factor of nearly six (Bailey 1993). Analytical data for earlier years are not available, but comparisons of application rates and river flows suggest that discharge concentrations between 1978 and 1981 were similar to those present between 1982 and 1985 for molinate and thiobencarb, respectively (see Table 1, Appendix C).

Other pesticides applied to rice have also been associated with toxicity. Bailey *et al.* (1994) showed that five pesticides out of approximately 20 applied to rice for at least five years between 1970 and 1989 were negatively correlated with striped bass recruitment. The pesticides were bufencarb (now discontinued), carbofuran, methyl parathion, molinate, carbaryl, and MCPA. With the exception of molinate and MCPA, these pesticides are cholinesterase inhibitors and would be expected to exert additive toxicity, a plausible scenario since most of these pesticides were applied in conjunction with each other. There also could have been effects on food organisms, which would have indirectly affected striped bass early life history stages. A model incorporating pesticide applications and river flows explained nearly 90 percent of the variation in recruitment during this period. One pesticide in particular, bufencarb, exhibited extremely high toxicity to striped bass embryos and larvae, with acute LC₅₀s of approximately 0.1 µg/L. At this level of toxicity, a daily input of 2400 g would be sufficient to render the Sacramento River acutely toxic at a flow rate of 10,000 cfs. This equates to approximately 150 lbs. over a 30-day period which is roughly 0.2 percent of the average amount applied annually between 1973 and 1981.

Application of carbofuran and methyl parathion to rice increased in 1980-1982 as bufencarb was being phased out; these data, along with Sacramento River flows between 1970 and 1988 are shown in Table 2, Appendix C. Although appreciable amounts were applied in prior years,

monitoring of carbofuran concentrations was not initiated until 1987. In that year, concentrations as high as 2.1 µg/L were detected in the Sacramento River during rice season (Menconi and Gray 1992). This value is clearly in excess of the water quality criteria of 0.5 µg/L recommended by CDF&G for the protection of aquatic life (Menconi and Gray 1992). The data in Table 2 regarding applications and flow rates suggest that 2.1 µg/L was potentially exceeded in six of the nine years between 1980 and 1988 and the criterion of 0.5 µg/L was exceeded back through 1977. More restrictive use requirements reduced carbofuran concentrations in the River to ≤ 0.5 µg/L by 1991 (Menconi and Gray 1992). Monitoring in the River and Delta between 1990 and 1992 by USGS suggests that carbofuran discharged from rice still reaches the Delta in trace concentrations (Kuivila *et al.* 1992). These data also suggest that Delta inputs of this pesticide, primarily from alfalfa, may also be significant. A half-life of three weeks in natural water suggests that concentrations of carbofuran may persist for a toxicologically significant period of time (Sharom *et al.* 1980).

Intermittent monitoring of methyl parathion concentrations in the Colusa Basin Drain and Sacramento River has occurred since 1980. In 1988 concentrations as high as 0.32 µg/L were detected in the Sacramento River. This value exceeds the recommended water quality criteria of 0.08 µg/L for the protection of aquatic life and also exceeds acute LC₅₀ values for *Daphnia magna* and *Neomysis mercedis* (Menconi and Harrington 1992). Based on applications and flow rates (Table 2, Appendix C), Sacramento River concentrations likely exceeded 0.32 µg/L in four of the nine years between 1980 and 1988. Using similar reasoning, the water quality criterion would have been exceeded in 15 of the 19 years between 1970 and 1988 (all of the years after 1976). Menconi and Harrington (1992) also concluded that levels of this pesticide could have exceeded the criterion during the early 1980s. Their reasoning was based on a 25 percent contribution from Colusa Basin Drain to the Sacramento River and measured concentrations of 3.7 µg/L in Colusa Basin Drain, which could have resulted in concentrations in the Delta of up to 0.94 µg/L, a level considerably greater than the acute LC₅₀ for *N. mercedis*. Monitoring data for 1990 suggest that more restrictive pesticide management practices have decreased River concentrations of methyl parathion to ≤ 0.1 µg/L (Menconi and Harrington 1992).

In 1991 and 1992, loadings of molinate and thiobencarb in the Sacramento River decreased by

over an order of magnitude from levels seen in previous years due to implementation of new pesticide management plans. However, in 1993, emergency releases from pesticide-treated fields prior to completion of the on-field holding time requirements resulted in the highest pesticide loadings to the River in five years, despite the fact that these releases were associated with < 3 percent of the total acreage treated. In fact, the loadings to the River probably were considerably higher than shown in the table since flows from Colusa Basin Drain, the largest single source of rice pesticides to the Sacramento River, were diverted into the River downstream of DPR's monitoring point for rice pesticides (DPR 1994). The fragile relationship between management practices and off-site movement of pesticides from rice culture is shown in the following table (data from DPR 1994) which clearly illustrates the effectiveness of the management practices in 1991 and 1992 and the sharp increase in molinate in the Sacramento River associated with the emergency releases in 1993.

Pesticides Transported in the Sacramento River Past Sacramento (kg)

<u>Year</u>	<u>Molinate</u>	<u>Thiobencarb</u>
1988	3194	68.1
1989	1984	11.4
1990	3204	51.2
1991	99	0
1992	57	0
1993	2007	0

For comparison, an estimated 18,465 kg molinate was transported in 1982 in the Sacramento River prior to onset of regulations designed to reduce offsite movement.

As an example of the effectiveness of the holding times, Regional Water Quality Control Board staff compared the toxicity of samples collected from discharges from fields undergoing emergency releases and from fields that had reached the required holding times (DPR 1994). Water samples from fields that had complied with the required holding times were not toxic to *C. dubia* while nine of ten tailwater samples collected from fields undergoing emergency releases were acutely toxic to *C. dubia*.

Pesticides entering the Sacramento-San Joaquin system are also associated with other types of agriculture, discharges from municipal sewage treatment plants, and storm water run-off. In two years of sampling the Delta, the three pesticides responsible for most of the observed toxicity were carbofuran, chlorpyrifos, and diazinon (Bailey *et al.*, unpublished data). These

pesticides occurred in locally high concentrations in smaller waterbodies or in large quantities of water moving through the Delta during major storm events.

Foe and Sheipline (1993) monitored watersheds associated with orchards in the Sacramento-San Joaquin Basin for toxicity during the dormant spray season between 13 January and 27 February. A total of 11 sites were monitored over 7 sampling events during this period. At least one sample collected from 9 of the 11 sites produced ≥ 50 percent mortality in *C. dubia*. Two, or more, samples collected from five of the sites produced total mortality in *C. dubia*. Of the 25 samples that exhibited significant mortality, diazinon was present in 22 samples at concentrations that exceeded the acute water quality criterion proposed by CDF&G (Menconi and Cox 1994). The median value was approximately 7 times the criterion, but concentrations as high as 6.8 $\mu\text{g/L}$ (over 80 times the criterion) were reached. Twenty-one of the samples contained concentrations that have been shown to cause acute mortality in *C. dubia* and six of the samples contained diazinon at concentrations lethal to *N. mercedis*.

An example of pesticide movement off-site into local receiving waters during irrigation and precipitation events is shown in a CDF&A study on diazinon applied in the lower American River watershed (Segawa and Powell 1989). In a three-year emergency program designed to eradicate the Japanese beetle, it was found that most of the diazinon was confined to upper layers of soil and thatch, but that significant off-site movement in irrigation water and stormwater run-off occurred. Concentrations as high as 73 $\mu\text{g/L}$ occurred in creeks receiving irrigation run-off and a concentration of 82 $\mu\text{g/L}$ were recorded in local streams following rainfall events. Rainfall events as low as 0.4-0.6 cm were sufficient to move significant quantities off-site. Mass discharge rates of 7.8 g/hour were recorded during irrigation and as high as 24 g per hour during rainfall events. During rainfall events, discharge rates as high as 5100 $\mu\text{g/sec}$ were measured. Following a rainfall event in Nov 1993, diazinon concentrations at nine sampling sites ranged between 0.4 and 44 $\mu\text{g/L}$. These values are from 1 to 110 times the acute LC_{50} for *C. dubia* and all exceeded the DF&G draft criteria for diazinon. The median concentration was 2.9 $\mu\text{g/L}$, 7.25 times the LC_{50} for *C. dubia* and 2.4 times the LC_{50} for *N. mercedis*. In spring 1984, concentrations in the streams ranged between 0.2 and 82 $\mu\text{g/L}$, with a median of 4.9 $\mu\text{g/L}$. Concentrations in Arcade Creek in fall 1984 during irrigation were between 0.7 and 11 $\mu\text{g/L}$, with a median of 6.4 $\mu\text{g/L}$. During rainfall events,

concentrations reached 21 $\mu\text{g/L}$, 52 times the LC_{50} for *C. dubia*. Although less diazinon was applied in 1985 and 1986, concentrations still reached 2 and 27 $\mu\text{g/L}$ in Arcade Creek in 1985 during irrigation and run-off periods, respectively. In 1986, rainfall events produced in-stream concentrations of up to 4.2 $\mu\text{g/L}$.

Using the fall (Aug - Oct) treatments as an example, Segawa and Powell (1989) estimated that an average of approximately 50 g/day was leaving the treatment areas via waterways, with peaks of up to 200 g/day. Assuming a uniform discharge rate, 50 g/day would have been sufficient to contaminate a flow rate of 51 cfs at the approximate *C. dubia* LC_{50} of 0.4 $\mu\text{g/L}$. During precipitation events, up to 24 g/hour was estimated to leave the treatment areas via waterways (18 g/hour in one creek!). Using similar reasoning, this amount would render a flow rate of 600 cfs acutely toxic to *C. dubia* or cause a flow of 3000 cfs to exceed the DF&G acute criterion for diazinon.

Kuivila (1993) tracked diazinon concentrations in the Sacramento River at Sacramento and in the San Joaquin River at Vernalis prior to and during rainfall events in early February 1993. On the Sacramento River, it was found that pulses of diazinon moved past the City of Sacramento 1-3 days after each rainfall event. Each pulse lasted 4-5 days. Diazinon peaks in the River reached 0.4 $\mu\text{g/L}$, compared with pre-event concentrations of 0.03-0.05 $\mu\text{g/L}$.

Kuivila (1993) also tracked one Sacramento River diazinon pulse downstream into the Estuary. The data suggest that diazinon concentrations peaked at Rio Vista and Chipps Island approximately 1- and 3 days after the pulse was recorded at Sacramento. Peak concentrations at Rio Vista and Chipps Island were 0.3 and 0.2 $\mu\text{g/L}$, respectively. It took an additional three days for the peak (now approximately 0.1 $\mu\text{g/L}$) to reach Martinez. The decreasing concentrations were due to tidally induced mixing. In addition, the peaks broadened as the pulse moved downstream. At Sacramento, concentrations in the Sacramento River exceeded 0.1 $\mu\text{g/L}$ for five days, compared with eight days at Chipps Island. All of these concentrations exceeded the acute diazinon criterion proposed by DF&G.

Unlike the Sacramento River, diazinon concentrations at Vernalis responded in bimodal peaks following the first rainfall event, suggesting upstream as well as local sources of diazinon (Kuivila 1993). Background concentrations of diazinon at Vernalis prior to and between storm

events were approximately 0.1 µg/L. In the first event (1.8 inches of rain), concentrations rose above 0.3 µg/L, with peaks of 0.8 and 1.1 µg/L, for eight days. The two subsequent events were much smaller, 0.7 and 0.6 inches, and resulted in 48- and 24-hour peaks of 0.3 and 0.2 µg/L, respectively. Similar data were also found in the San Joaquin River at Stockton during the same events. All of these concentrations exceeded the draft acute criterion for diazinon proposed by DF&G.

In contrast to the pulses observed on the San Joaquin River, diazinon concentrations at sites on the Old and Middle Rivers increased steadily from 0.04 to 0.15 µg/L during this same period (Kuivila 1993). These latter sites do not have a pronounced downstream flow gradient and are heavily influenced by tidal movements. All of these measurements were at or exceeded the chronic criterion proposed by DF&G and some also exceeded the acute criterion.

In terms of toxicity, 100 percent mortality was observed with *C. dubia* exposed to samples collected daily from the San Joaquin River at Vernalis for twelve days following the first event (Kuivila 1993). Diazinon concentrations in these samples were ≥ 0.15 µg/L. Other pesticides, including chlorpyrifos, methidathion, and carbaryl may also have contributed to toxicity in these samples. No toxicity was observed in samples that contained ≤ 0.08 µg/L diazinon.

The USGS also monitored pesticides in the Sacramento River at Sacramento and in the San Joaquin River at Vernalis between 1 December 1993 and 28 February 1994 (MacCoy 1994). A total of 124 samples were collected, divided almost equally between the Sacramento River and San Joaquin Rivers. Diazinon was not detected in 26 percent of the samples collected from the Sacramento River. Thirty-four percent of the samples exceeded the draft CDF&G 4-day average criterion (chronic) of 0.04 µg/L diazinon, and 13 percent of the samples exceeded the 1-hour criterion (acute) of 0.08 µg/L. The results were very similar for the San Joaquin River where diazinon concentrations exceeded the draft chronic and acute water quality criteria in 44 and 16 percent of the samples, respectively, and was not detected in 33 percent of the samples. Chlorpyrifos was not detected (0.025 µg/L = detection limit.) in any of the samples, but other pesticides were found, most notably simazine (to a maximum value of 1.7 µg/L) and methidathion (up to 1 µg/L). Generally, elevated concentrations of pesticides appeared in fairly distinct pulses that lasted between three and ten days.

Interestingly, the amount of diazinon transported in the Sacramento River during these February events was much higher than in the San Joaquin River. Even though maximum concentrations were approximately 2.5 times higher at Vernalis than in the Sacramento River, flows in the Sacramento were 10 to 15 times greater than in the San Joaquin River (Kuivila 1993). Depending on the interactions between pesticide applications, rainfall events, and flow, much higher concentrations could be carried in the Sacramento River into the Delta. Since average flows in the Sacramento River in February between 1987 and 1991 were 12,800 cfs (CV=24.5%), compared with the 40,000-60,000 cfs that occurred during this study, it would appear that the potential exists for substantially higher concentrations to occur in the Sacramento River than measured in February of 1993.

This analysis is supported by data collected in February 1994 by DPR (V. Connor, CVRWQCB, personal communication). In this study, diazinon concentrations as high as 0.7 $\mu\text{g/L}$, nearly nine times the proposed acute water quality criterion, were measured in the Sacramento River following a rainfall event of 1.6 inches in four days. River flow rate varied between 12,000 and 30,000 cfs during this period.

Menconi and Cox (1994) presented monitoring data for diazinon collected from 47 sites in the Sacramento-San Joaquin system between March 1991 and February 1993. A total of 340 samples were collected. Measured concentrations ranged between 0.01 and 36.8 $\mu\text{g/L}$ diazinon. A total of 104 (30.6 %) samples exhibited diazinon concentrations that were less than the draft chronic water quality chronic criterion. 170 of the samples (50 %) exceeded the acute criterion and the remainder exceeded the chronic criterion. All of the samples collected at Freeport/Rio Vista (n=4), Vernalis (n=6), and Chipps Island/Martinez (n=3) exceeded the acute criterion of 0.08 $\mu\text{g/L}$.

In their water quality document for chlorpyrifos, Menconi and Paul (1994) presented monitoring data collected from sites in the San Joaquin system between March 1991 and February 1993. Of the 25 sites sampled, chlorpyrifos concentrations exceeded the criterion at 17 sites. Of the sites that were sampled at least five times, only the Stanislaus River consistently exhibited chlorpyrifos concentrations less than the criterion. Six of the 45 samples

collected from the San Joaquin River exceeded the LC₅₀ for *C. dubia*. Concentrations as high as 0.35 µg/L were recorded from the San Joaquin River; this value exceeds the LC₅₀s for *C. dubia* and *N. mercedis* by factors of 5 and 4, respectively.

A total of 50 water samples were collected across 12 sites in the Delta between July 1993 and March 1995 and analyzed for carbamate and organophosphorous pesticides (Bailey *et al.*, unpublished). Water quality criteria for diazinon, carbofuran, and/or chlorpyrifos were exceeded in 43 (86 percent!) of the samples. Maximum concentrations were 0.37, 4.8, and 0.896 µg/L for diazinon, carbofuran, and chlorpyrifos, respectively.

Diazinon concentrations exceeded the criteria in all four samples analyzed from the San Joaquin River at Vernalis between 9 and 13 January 1995 (Deanovic *et al.* 1995). Two of the three samples analyzed from the Sacramento River at Greene's Landing during this same time period also contained diazinon at concentrations in excess of the criteria.

Gilliom and Clifton (1990) reported total DDT concentrations of 0.01-0.08 µg/L in water samples collected from the San Joaquin River at Vernalis. These values exceeded the EPA 24-hour water quality criterion by factors of 10-80. Based on sampling conducted in 1985, Gilliom and Clifton concluded that concentrations of organochlorine pesticides in bed sediments of the San Joaquin River were among the highest measured in major rivers in the United States.

Lartiges and Garrigues (1995) evaluated the half-life of a number of triazine, carbamate, and organophosphorous pesticides, including diazinon. The parameters varied included water type, temperature, and light. As part of the justification of their study, the authors noted that half-lives of 120 and 170 days have been shown for chlorpyrifos and parathion. A half-life of 200 days was found for parathion in estuarine water. Chemical degradation predominates for chlorpyrifos, which may explain its relatively long-term presence in samples collected in winter months (the dormant spray season). In addition, chlorpyrifos is frequently present absorbed to particulates, a factor that may increase its persistence in the environment. For diazinon, half-lives at 6°C ranged from 125 to 181 days, irrespective of water type (ultra-pure, river water, filtered river water or seawater). At 22°C, half-lives were much shorter, between 50 and 80 days. The half-life in filtered river water was approximately 30 percent shorter than in

unfiltered river water, again suggesting that sorption reduces the degradation rate. Sunlight did not influence the degradation rate in seawater, but did reduce the half-life by approximately 50 percent in river water. pH between 6.1 and 8.1 did not appear to affect degradation. Atrazine was comparatively refractory to degradation. No degradation was observed in ultra-pure water at either 6 or 22°C, or in sea water or filtered river water at 6°C. In river water, the half-life was 235 days at 6°C and 164 days at 22°C. Sunlight further reduced the half-life to 59 days. By comparison, sunlight had very little effect on the degradation rate of atrazine in seawater (half-life of 169 days) compared to a half-life of 200 days at 22°C in the dark.

Atrazine concentrations were monitored in surface run-off and in tile drainage (Gaynor *et al.* 1995). Concentrations in surface run-off were nearly twice as high as in tile drainage. Concentrations also varied with the type of tillage. However, the greatest reduction (60 to 80 percent) in offsite movement occurred by applying the herbicide in bands directly over the seeded rows compared with standard broadcast methods which also apply the herbicide to the furrows. Maximum concentrations of 700 µg/L were recorded in surface run-off using the broadcast method compared with 140 µg/L with the banded application. These results demonstrate the potential effectiveness of "best management practices" with respect to reducing pesticide concentrations in receiving waters.

Pesticide applications can also affect avian species. Littrell (1988) reported deaths of waterfowl and raptors associated with carbofuran poisoning in the Sacramento Valley between 1984 and 1988. Carbofuran use increased following the withdrawal of bufencarb (BUX) from the market. Carbofuran residues were found at concentrations of up to 640 ppm (wet weight) in gizzards and crops of dead birds, and brain cholinesterase levels were decreased by up to 86 percent. Male birds were characterized by a prolapsed penis, a characteristic of carbamate and organophosphorous poisoning. The ducks were poisoned by feeding on carbofuran applied in a granular form. The raptors appeared to have been affected indirectly by feeding on poisoned ducks. Losses occurred in both spring and fall; the absence of registered uses in the fall indicated that illegal applications occurred. To reduce or eliminate these losses, application methods were modified to include incorporation of the granules into the soil prior to flooding.

During the CDF&A program to eradicate the Japanese beetle, nine confirmed bird kills (no

numbers given) were reported as a result of the diazinon treatments in fall 1983 (Segawa and Powell 1989).

Inorganic contaminants, generally mobilized from soils by irrigation and drainage activities, are also associated with agricultural practices. Saiki *et al.* (1993) evaluated boron, molybdenum, and selenium in aquatic organisms in the lower San Joaquin drainage. Concentrations of boron and selenium were elevated in reaches that received tile drainage from irrigated agriculture. Boron and molybdenum were not biomagnified in food chain. Selenium appeared to be biomagnified. Selenium concentrations in some areas in fish reached 23 $\mu\text{g Se/g}$ body weight (dry weight), twice as high as needed to elicit reproductive effects. Boron levels were also somewhat elevated. Chinook salmon and striped bass fingerlings accumulated up to 200 $\mu\text{g/g}$ boron after 28 days of exposure to tilewater and also exhibited poor survival. Threshold selenium concentrations associated with reproductive failure in fish include: 2-5 $\mu\text{g/L}$ in water, 4 $\mu\text{g/g}$ in sediment, 5 $\mu\text{g/g}$ in food, and 12 $\mu\text{g/g}$ in whole fish. Whole fish concentrations as low as 3-8 $\mu\text{g/g}$ reduced growth and survival in juvenile chinook salmon. The authors concluded that any increase in tile drainage to the San Joaquin River will further increase adverse effects on fish.

Saiki *et al.* (1992) evaluated selenium and other elements in freshwater fish from different sites in the San Joaquin valley. Arsenic, mercury, and selenium were elevated in fish from one or more sites, but no evidence for accumulation of chromium was obtained. Tissue concentrations of selenium were high enough in some cases to adversely affect survival, growth and reproduction. The distribution of elevated selenium concentrations coincided with inputs of tile drainage to the San Joaquin River, primarily through Salt and Mud Sloughs. The data suggested that selenium concentrations peaked in 1984 and have declined slightly since. Changes in agricultural practices could reverse this decline. Fish collected just downstream of the confluence of the Stanislaus River exhibited body burdens of selenium that ranged between 1.3 and 1.8 $\mu\text{g/g}$ dry weight. The values were similar for mosquito fish, bluegill, carp and largemouth bass. Much higher levels were seen in Salt and Mud Sloughs (up to 11 $\mu\text{g/g}$), and even higher concentrations were found in the mid-1980s (up to 23 $\mu\text{g/g}$). The data suggest that the problem currently is relatively local, although more selenium may have been exported in the past. Chinook salmon and striped bass exposed to tile water accumulated selenium and

exhibited reduced growth. This could be a problem if selenium concentrations increase as a function of increased tailwater discharges into the river.

Most of the selenium entering the Bay and Delta is from the Sacramento River except during periods of high flows when the San Joaquin River, which typically carries much higher selenium loadings than the Sacramento River, enters the Bay. During low flow periods, selenium loading from the rivers averages 0.87 kg/day. During high flow periods, riverine inputs average 3.4 kg/day. In comparison, the oil refineries in the vicinity of Carquinez Strait discharged approximately 7.1 kg/day in 1991, and all of the POTWs combined totalled 2.4 kg/day (of this, approximately 0.4 kg/day is discharged into the South Bay). Proposed emissions controls have focused on the refineries due to the large inputs. Most of the selenium entering the South Bay comes from POTWs and an effective control strategy has not yet been identified (Taylor *et al.* 1993).

Taylor *et al.* (1992) prepared a mass emissions reduction strategy for selenium in the Bay. They concluded that selenium enrichment was occurring in food chains in Suisun Bay, Carquinez Strait, eastern San Pablo Bay and the South Bay. Because of selenium's propensity to accumulate through the food chain, the approach involved reducing total mass emissions of selenium by 90 percent over a nine-year period. This goal would reduce anthropogenic selenium emissions to a level comparable to loading from the major rivers during low-flow periods. Most of the selenium in the North Bay originates from six oil refineries (non-agricultural point sources) and has resulted in a human health advisory for diving ducks from this area. In addition to human health concerns, selenium concentrations in the duck liver tissues (14–209 µg/g dry weight) overlap or exceed those concentrations that adversely affected ducks at Kesterson Reservoir (46–82 µg/g). In addition, the maximum concentration found to date in California clapper rail eggs (7.3 µg/g dry weight) is very close to the 8 µg/g threshold associated with reduced hatching success in other birds. Clam tissues from North and South Bays also contain elevated selenium concentrations (2.8–5.2 µg/g dry weight) that are approximately twice normal background levels. There is also concern about selenium concentrations in white sturgeon muscle (6–9 µg/g dry weight) and in whole body preparations from striped bass (7.9 µg/g dry weight). Concentrations in both of these species are comparable to the range (8–12 µg/g) associated with adverse effects in other species. The report suggested that 0.7 (or 0.45 as organic selenium), 1.5, and 3.2 µg/g were appropriate

threshold guidelines for concern in aquatic plants (including algae), sediments, and bivalve tissue, respectively (Taylor *et al.* 1992 and 1993).

Horne (1991) evaluated the effects of permanent flooding of selenium-contaminated lands in the San Joaquin drainage on selenium concentrations. Permanent flooding rendered selenium unavailable as an insoluble fraction in anoxic sediments, thus making it biologically immobile. Selenium concentrations in *Chara* (macro alga), an herbivorous chironomid, and a predaceous damselfly were monitored following flooding. Rapid initial declines in selenium concentration were followed by a continued long term decrease. Decreases were noted in water column concentrations and in organisms over the 2.3 year study period. Between 85 and 93 percent of the initial selenium was lost; no difference was seen between the herbivore and predator. Concentrations in *Chara* dropped to 3-4 ppm and to 14-15 ppm in the insects.

Urban Stormwater Inputs

In the spring of 1993, Hansen and Associates (1994) investigated toxicity associated with stormwater in the San Lorenzo Creek watershed which enters San Francisco Bay just north of Hayward. Samples were collected from 3-5 sites in the watershed following three precipitation events. Diazinon concentrations at the sites ranged between 0.74 and 2.9 $\mu\text{g/L}$ for samples collected 16 March, between 0.82 and 2.9 $\mu\text{g/L}$ for samples collected 17-21 March, and between 0.08 and 0.46 $\mu\text{g/L}$ in samples collected 7 April. With the exception of the sample that contained 0.08 $\mu\text{g/L}$, all of the measured concentrations exceeded values associated with acute toxicity in *C. dubia* and two of the values exceeded the acute LC_{50} for *N. mercedis*. All of the values exceeded the proposed CDF&G acute and chronic water quality criteria for diazinon.

In the fall and winter of 1994-1995, stormwater samples were collected from creeks and sumps discharging into the lower Sacramento and American Rivers (Bailey *et al.* unpublished data). Samples collected from Arcade, Elder, and Strong Ranch Creeks following multiple precipitation events all exhibited acute toxicity to *C. dubia*. In all cases, toxicity was removed by treatment with piperonyl butoxide, a biochemical that inhibits the toxicity of metabolically activated organophosphorous pesticides. Diazinon was found at acutely toxic concentrations in

all three creeks and chlorpyrifos was found at acutely toxic concentrations at 1 of the 3 sites. In one of the two sumps, diazinon and chlorpyrifos were both present at acutely toxic concentrations, but metals also contributed to toxicity. In the remaining sump, toxicity was driven by high zinc concentrations. Algal cell numbers were also reduced when exposed to the stormwater samples. Stormwater samples collected during the 1993–1994 season also produced mortality in exposed fathead minnow larvae.

Sites that drained into the San Joaquin River in the vicinity of Stockton also exhibited acute toxicity to *C. dubia* and to the algae over multiple testing events (Bailey *et al.* unpublished data). These sites included the Calaveras River, Smith Canal, and Mosher Creek. A fish kill was also observed in the Calaveras River during the first precipitation event of the season.

Concentrations of diazinon and chlorpyrifos in samples collected during wet and dry periods events from creeks and sloughs in the vicinity of Sacramento and Stockton were analyzed with ELISA between December 1994 and March 1995 (Bailey *et al.* unpublished). All of the sites sampled drained into the lower American River, the Sacramento and San Joaquin Rivers, or directly into the Delta. Approximately 210 samples were analyzed for diazinon, and over 85 percent of the samples contained diazinon at concentrations exceeding the proposed CDF&G water quality criteria for this pesticide. Approximately 70 samples were analyzed for chlorpyrifos and nearly 90 percent of these exhibited concentrations in excess of the water quality criteria proposed by CDF&G for this pesticide. Of the 47 samples tested for toxicity with *C. dubia*, 36 exhibited acute toxicity.

Concentrations of diazinon and chlorpyrifos were also measured with ELISA between December 1994 and April 1995 in creeks tributary to San Francisco Bay (Bailey *et al.* unpublished). Diazinon concentrations in approximately 175 samples were determined and exceeded the CDF&G water quality criteria in nearly 74 percent of the samples. Chlorpyrifos concentrations were determined in 70 samples. Of these, approximately 70 percent contained chlorpyrifos at concentrations that exceeded the CDF&G water quality criteria for this pesticide. None of these samples were tested for toxicity.

High concentrations of these pesticides were also found in rain and fog samples collected in the

Sacramento Valley, suggesting that atmospheric transport may be an important mechanism for the distribution and deposition of these pesticides (Connor *et al.* unpublished). This observation may account for the overall higher proportion of these pesticides in stormwater run-off in the Sacramento and Stockton sites compared with the San Francisco Bay Area sites; most of the Valley sites are located in storm paths that pass over agricultural areas and accumulate a pesticide load. In contrast, there is relatively little pesticide application to the west of the Bay Area; therefore, concentrations measured in Bay Area creeks may reflect local applications while those measured in the Valley sites reflect local inputs as well as atmospheric deposition.

Point-Source Inputs

Sewage outflows can be a significant component of local water regimes. For example, the South Bay receives 10 percent of the annual river run-off, but 76 percent of the Bay's total annual inflow of wastewater (Conomos 1979). An Effluent Characterization Program was initiated with dischargers into San Francisco Bay by the San Francisco Bay Regional Water Quality Control Board. Under this program, dischargers were required to regularly monitor the acute and chronic toxicity of their effluent for approximately 12 months. Sampling intervals were generally monthly, with intensive weekly testing conducted for short periods of time. Both marine and freshwater species were used, the species selected depended on their sensitivity during a screening phase of testing.

Data from these studies are summarized in Appendix B, which includes the test species, the number of samples tested and the number that produced toxicity. The results are from 33 dischargers, including 22 POTWs, 5 oil refineries, one steel mill, 3 cooling systems, and 2 chemical companies. In 1994, these dischargers produced a total daily average flow of approximately 1,360 million gallons to the Bay (L. Tang, San Francisco Bay Regional Water Quality Control Board, personal communication). Acute toxicity was determined on the basis of ≥ 30 percent mortality within the first 4 days of exposure in 100 percent (or the highest concentration tested) effluent. Chronic toxicity was determined on the basis of the no-observable effect concentration (NOEC) from the effluent dilution series being \leq to the estimated dilution in the receiving water after mixing. The estimated dilution was taken to be 10 percent for deep-water dischargers and zero (no dilution) for shallow water dischargers.

As shown in the following summary tables, evidence of acute and chronic toxicity was found for most of the dischargers evaluated.

<u>Percentage of Effluent Samples Exhibiting Acute Toxicity</u>					
	<u>< 20%</u>	<u>≥ 20%</u>	<u>≥ 30%</u>	<u>≥ 40%</u>	<u>≥ 60%</u>
No. of Dischargers	8	21	16	14	11

<u>Percentage of Effluent Samples Exhibiting Chronic Toxicity</u>					
	<u>< 20%</u>	<u>≥ 20%</u>	<u>≥ 30%</u>	<u>≥ 40%</u>	<u>≥ 60%</u>
No. of Dischargers	2	31	26	21	11

Two thirds of the dischargers exhibited acute toxicity at least 20 percent of the time and one-third exhibited acute toxicity over 60 percent of the time. Virtually all of the dischargers exhibited chronic toxicity at least 20 percent of the time and one-third exhibited chronic toxicity over 60 percent of the time. Limited TIE results suggested that ammonia, metals and organophosphorous pesticides contributed to toxicity.

Currently, chronic testing has been imposed on comparatively few dischargers and at a relatively low frequency. The problem with reduced testing frequency is that the likelihood of capturing episodic or seasonal events is low and, even if found, is likely to be dismissed as a false positive event. It is also difficult to confirm toxicity with a TIE unless the toxic event is followed up immediately. Low sampling frequency also implies that each discharger exhibits relatively low variability; unfortunately, continually changing inputs alter the nature and frequency of toxicity. In addition, acute toxicity tests may be required at more frequent intervals but a fish is generally selected as the test species in spite of evidence from the Effluent Characterization Program that may have identified invertebrates toxicity as the most sensitive indicator of acute toxicity. In these cases, it would be appropriate to include the invertebrate in the acute toxicity test battery.

Metabolically activated organophosphorous pesticides were found to be responsible for acute toxicity to *C. dubia* in 10 of 14 toxic samples collected from an 150 mgd (million gallons daily

discharge) publicly owned sewage treatment plant that discharges into Suisun Bay (AQUA-Science 1992). A Toxicity Identification Evaluation demonstrated that diazinon was the primary toxic constituent and chlorpyrifos also contributed to toxicity. Other investigators have also demonstrated that diazinon may be present at acutely toxic concentrations in municipal effluents (Amato *et al.* 1992; Burkhard and Jensen 1993).

A study conducted on five POTWs that contribute a total daily flow of approximately 235 mgd to the Estuary suggests that the potential for toxicity due to pesticides may be widespread in municipal effluents discharged into the Estuary (Miller *et al.* 1994). Based on weekly samples collected for a 6-week period, all of the POTWs contained measurable levels of chlorpyrifos and diazinon in their influent and effluent streams. During this period, four of the five plants produced at least one sample that had diazinon concentrations in excess of levels associated with acute *C. dubia* LC50s. Samples from three of the five plants contained chlorpyrifos at acutely toxic concentrations. The plants varied markedly in the removal efficiencies associated with the pesticides, particularly with respect to chlorpyrifos, which suggests that toxic concentrations may be treatable within the context of plant operation.

Surfactants have also been shown to cause toxicity in municipal effluents, but the extent of this problem has not been characterized locally (Ankley *et al.* 1990).

Smith and Bailey (1990) investigated attraction and avoidance of anadromous fish to refinery (San Francisco Bay) and municipal (Russian River) effluents. The test species included steelhead, striped bass, and Chinook salmon. Both attraction and avoidance responses to refinery effluent were noted, depending on concentration. Responses were found at dilutions as low as 1000:1. At concentrations of $\leq 100:1$, attraction was noted for all three species. Results appeared to be validated by field observations; for striped bass, juvenile fish found in the slough that received the discharge exhibited eroded fins, suggesting adverse effects coupled with lack of avoidance response. Adult salmon were also frequently found in the slough that received the discharge. Steelhead were the only species tested with domestic effluent; in contrast to the attractant response to refinery effluent, strong avoidance to the POTW discharge was noted. Subsequently, operation of POTW treatment plant was modified to permit intermittent discharge during steelhead migration.

Refinery effluents have also been shown to cause toxicity at concentrations lower than those achieved by deep water discharge (10 percent effluent) in San Francisco Bay. Chapman *et al.* (1994) evaluated the toxicity of refinery waters to a variety of aquatic organisms and reported a wide range of sensitivities. Some species of fish and invertebrates were adversely affected at \leq 10 percent effluent. The authors also noted eroded fins on exposed fish. Weiss *et al.* (1989) found effects on winter flounder, striped bass, and mummichog at 10 percent effluent (growth and development). With fathead minnows, DeGreave *et al.* found NOECs of 0.5 and 21.6 percent for two oil refinery effluents.

Sediments

Swartz *et al.* (1994) compared sediment toxicity, contamination and amphipod abundance at a Superfund site in San Francisco Bay. At this site, the Lauritzen and Santa Fe Channels and part of Richmond Inner Harbor have been contaminated with DDT and dieldrin. Property adjacent to the sites was used to formulate DDT and dieldrin from 1945 to 1966. In some areas, largely removed in 1990, banks along the Lauritzen Channel contained virtually 100 percent DDT. Sediment pesticide concentrations were highest in Lauritzen Channel, decreasing through the Santa Fe Channel to Richmond Inner Harbor. Sediment samples were evaluated for toxicity with the amphipod *Eohaustorius estuarius*, analyzed for concentrations of contaminants, and compared with respect to amphipod abundance and diversity in the field. Except for one site in the Santa Fe Channel with high PAH levels, concentrations of PAHs, PCBs, and metals were not high enough to cause toxicity. Threshold sediment toxicity occurred at 300 μg DDT/g organic carbon (OC) for *E. estuarius* and at 100 μg DDT/g OC for the naturally occurring populations of amphipods. One species of local amphipod, *Grandidierella japonica*, appeared to be tolerant of elevated DDT concentrations. Average mortalities for *E. estuarius* were 42, 30 and 24 percent in samples collected from the Lauritzen Channel, Santa Fe Channel and Richmond Inner Harbor, respectively. Only sites in the Lauritzen Channel contained sufficient DDT to account for mortalities. The interstitial water threshold concentration of DDT was 0.5 $\mu\text{g/L}$, with 10-day LC_{50} of 2.2 $\mu\text{g/L}$. Pinza *et al.* found toxicity to another amphipod *Rhepoxynius abronius* in sediment samples collected from the southeastern bank of the Richmond Inner Harbor Channel. Data from both studies suggest that contamination and associated toxicity were patchy; sites in Lauritzen Channel only

meters apart produced a range of 35 - 100 percent mortality. Similarly, samples collected from 26 sites in the South Bay produced an average of 45 percent mortality in *R. abronius*, with a range of 20-100 percent.

Long *et al.* (1990) evaluated toxicity of sediments from San Francisco Bay with a variety of species. Three samples were from Oakland Inner Harbor (OIH), and three each from Yerba Buena, Vallejo and San Pablo. Tests included elutriate tests with mussel (*M. edulis*) and sea urchins (*S. purpuratus*), solid phase sediment tests with amphipods (*R. abronius* and *A. abdita*), and pore water tests with the polychaete (*Dinophilus gyrociliatus*). Reduced survival ($\leq 45\%$) was seen with *R. abronius* in all three OIH samples, 1 of 3 Vallejo samples, and 1 of 3 samples from San Pablo. The response in samples from different sites at Yerba Buena was more uniform and averaged about 65 % survival compared with 95% in controls. With *A. abdita*, only one of the OIH samples reduced survival and no effects on survival were seen in samples from the other sites. With *M. edulis*, reduced larval survival was seen in all of the samples from OIH, 2 of 3 from Yerba Buena, 1 of 3 from Vallejo and 1 of 3 from San Pablo. Larval abnormalities were also evaluated with this test; they were less than 25 % in all samples. With the sea urchins, there were no effects on normal development, but mitotic aberrations, micronucleated cells, and cytologic abnormalities were elevated in samples from all sites compared with the controls. With the polychaete, none of the samples reduced survival, but eggs per female were reduced in 2 of 3 of the samples from OIH and in all of the samples from Yerba Buena. Chemical analyses indicated that PAHs, DDT, total chlorinated pesticides, and PCBs were elevated in OIH samples compared with other sites. The Vallejo sites had lower PAHs than other sites. All of the San Francisco Bay sites had higher levels of these contaminants than samples from Tomales Bay. Correlations with different contaminants suggested that different organisms often responded to different contaminants. Ammonia and hydrogen sulfide may also contribute to sediment toxicity (Ankley *et al.* 1992), but potential effects of these toxicants have not been thoroughly investigated locally.

SPECIES EFFECTS

It is generally accepted that numerous terrestrial and aquatic vertebrate, invertebrate, and algal species found in the Delta have declined in abundance over the past 20 years (Herbold *et al.*

1992). These declines have been attributed to a number of causes, including reduced habitat, reduced freshwater outflows, increased diversions, and introduced species, which have led to lower overall abundance of many species found in the Delta. Although adverse effects associated with toxic pollutants has been suggested as potentially contributing to the decline of species in the Estuary, comparatively little work has been done on species found in the Delta with respect to the effects of toxic substances. Studies that pertain to species of interest are described below.

Invertebrates

***Neomysis mercedis*:** *N. mercedis* is a small crustacean found in estuaries along the Pacific Coast. It is widely distributed in the Delta where it is a very important dietary component of larger invertebrates and juvenile fishes (Heubach 1969 and 1972; Orsi and Knutsen, 1979). Bailey (1993) evaluated the acute and chronic toxicity of the rice herbicides molinate and thiobencarb to *N. mercedis*. The data indicated that the two herbicides were additive in toxicity. Furthermore, comparison of measured concentrations of these pesticides in the Delta in 1985 with chronic toxicity values suggested that these pesticides may have reached toxic levels during that year. It is likely that concentrations were even higher in preceding years. Although no analytical data are available for the Delta for the years prior to 1985, known pesticide application levels, shorter on-field holding times, lower river flows, and higher measured concentrations in Colusa Basin Drain all would have contributed to higher concentrations in the Delta. For example, in excess of 5 chronic TUs could have been reached in the Delta during the 1982 rice season (Bailey 1993). Increased on-field holding times have reduced concentrations of these two pesticides in receiving waters in subsequent years (DPR 1994).

Bailey *et al.* (1994b) evaluated the sensitivity of *N. mercedis* to samples from Colusa Basin Drain. Ten of the 14 samples collected from CBD during rice season in 1989 produced complete mortality within 24 hour. Follow-up testing in 1990 indicated that the primary cause of toxicity was the organophosphorous pesticide methyl parathion (Finlayson *et al.* 1993). Reduced toxicity was observed in 1991 and was attributed to increased on-field holding time requirements for this pesticide (Bailey *et al.* 1994b). In a hazard assessment on methyl

parathion prepared by California Department of Fish and Game, Menconi and Harrington (1992) pointed out that cladocerans and mysids, two important components of the Delta food chain, were among the most sensitive species to this pesticide. They also pointed out that, based on measured concentrations in CBD and flows in the Sacramento River, concentrations of this pesticide could have exceeded the current water quality guidelines in the Delta in the early 1980s before stricter regulations were enforced. Their calculations show that nearly 1 µg/L methyl parathion could have been present in the Sacramento River downstream of Sacramento for up to four weeks. This value is five times higher than the 96-hour LC₅₀ for *N. mercedis*. In 1988, analytical measurements made in the Sacramento River near Sacramento, showed that concentrations as high as 0.32 µg/L existed; this value exceeded the LC₅₀ for *N. mercedis* by a factor of 1.5. Note that these concentrations would likely have reached the Delta largely unchanged since any further dilution would have occurred primarily through the relatively slow process of tidal mixing (Kuivila and Foe 1995).

The following acute toxicity values for carbofuran, diazinon, and chlorpyrifos were obtained with *N. mercedis* (Bailey *et al.* accepted, Brandt *et al.* 1993):

<u>Pesticide</u>	<u>96-hour LC₅₀ (µg/L)</u>
carbofuran	2.7-4.7
chlorpyrifos	0.07-0.09
diazinon	1.2-1.9

Monitoring data from different sites in the Delta suggest that these values are exceeded regularly, with the frequency depending on the pesticide. For example, Foe and Sheipline (1993) reported diazinon values in 26 samples collected from waters entering the Delta in January and February 1992. Concentrations in seven of the samples exceeded the LC₅₀ for *N. mercedis* and concentrations in nearly half of the samples exceeded the acute NOEC.

Collectively, the data suggest that pesticide concentrations in the Delta have regularly exceeded levels associated with acute and chronic toxicity to this species, as well as their respective water quality criteria. Although the identity of the pesticides has changed somewhat over time, the available data suggest that elevated pesticide concentrations have been a significant issue in Delta and tributary waters since the mid-1970s.

Bivalves: Pereira *et al.* (1992) reported on bioaccumulation of hydrocarbons in the introduced clam *Potamocorbula amurensis* in Suisun Bay. Bioaccumulation of sediment hydrocarbons originating from petroleum sources was identified as was accumulation of polycyclic aromatic hydrocarbons derived from combustion. This species is a food source for a number of species including sturgeon and diving ducks.

Luoma *et al.* (1990) evaluated temporal variation in trace metals in the introduced clam *Corbicula* in Suisun Bay and near the mouth of the San Joaquin River over a three year period. The authors concluded that there was little chronic contamination associated with silver, zinc, or lead; but that substantial chronic contamination was present in Suisun Bay with respect to copper, cadmium, and chromium. Inputs of chromium were dominated by discharges from a local steel mill, and copper appeared to originate primarily from the Sacramento River during high inflows to the Bay. Sources of cadmium were attributed to both riverine and local sources. The condition factor of clams in areas with highest contamination was reduced as was the abundance of larger clams. The data suggested that the bioavailability of copper and cadmium to the clams was greater in Suisun Bay than reported in other estuaries. In fact, tissue concentrations of copper in clams from Suisun Bay were 6-10 times greater than reported in un-enriched systems and tissue concentrations of cadmium were found that exceeded levels reported anywhere in the literature. Some of the cadmium tissue concentrations exceeded guidelines for human health consumption. Chromium concentrations in clam tissue were equal to the highest literature values found.

Leland and Scudder (1990) looked at tissue metals concentrations in *Corbicula* in the San Joaquin River. Selenium concentrations varied directly with soluble selenium in riverwater. Selenium entered the system through subsurface drain and irrigation tailwaters. Elevated concentrations of mercury, arsenic, copper, cadmium and nickel were also found, although the concentrations varied with respect to location and source. Boron and molybdenum were not accumulated and chromium, lead, silver, vanadium, and zinc exhibited little geographic variability in tissue concentrations. The authors concluded that there was no evidence of synergism or antagonism between As, cadmium, copper, mercury, nickel, and selenium with respect to their uptake. Based on their data, the authors found that available cadmium, copper,

and nickel were not enriched compared with other sites. Mercury was elevated in the tributaries and one site in the lower San Joaquin River, and selenium was elevated primarily in the southern San Joaquin River and in tributaries that drained the western side of the Valley. Arsenic was enriched in the San Joaquin river and tributaries. Johns *et al.* (1988) reported selenium concentrations in the western Delta and Suisun Bay were elevated compared with sites in the southern Delta and lower Sacramento River. These were attributed to industrial discharges (nine of the largest point source dischargers in the Bay/Delta system release directly into Suisun Bay (Gunther *et al.* 1987). The major contribution of the San Joaquin River to Delta metal loads (aside from effects on productivity, nursery areas, etc., within the San Joaquin River) occurs in spring when discharge is high and water exports are minimal.

Crayfish: Holck and Meek (1987) reported the LC₅₀ of the crayfish *Procambarus clarkii* exposed to the pyrethroid insecticide, resmethrin, to be 0.82 µg/L.

Naqvi and Newton (1991) examined the toxicity of endosulfan (Thiodan) to the Louisiana Red Crayfish (*Procambarus clarkii*). Endosulfan exhibited a half-life of 2+ years in sandy loam soil. The data suggested effects at concentrations as low as 2 µg/L, but the small sample size and high variability preclude separating means.

Tadpole shrimp: Walton *et al.* (1990) evaluated the toxicity of four pesticides to tadpole shrimp (*Triops longicaudatus*). The following 24-hour LC₅₀s (in µg/L) were obtained : 4.0 (chlorpyrifos); 73.8 (fenthion); 0.084 (cypermethrin); and 0.7 (resmethrin). In field studies, the lowest effective concentrations were (in g/ha): 11 (chlorpyrifos-EC 4); < 56 (fenthion-EC 4); 1-3 (cypermethrin-EC 2.5); and < 28 (resmethrin-18%).

Fairy shrimp: Mizutani *et al.* (1991) evaluated the uptake of lead, cadmium and zinc by fairy shrimp *Branchinecta longiantenna*. These shrimp inhabit temporary rain pools. Organisms tolerated 25 mg/L Pb for two days, but 1 mg/L Cd or Zn was lethal. At 15 mg/L Pb or 0.1 mg/L Cd or Zn, exposed organisms died within 6-8 days. *B. longiantenna* accumulated all three metals which may be a source of concern since this species can be a significant source of food for migratory birds. Also, brine shrimp *Artemia salina*, which are widely distributed in salt ponds and consumed by birds, accumulate cadmium to 100 mg/kg wet weight (Jennings and Rainbow 1979).

Aquatic insects: Taylor *et al.* (1991) evaluated the effect of 3,4-dichloroaniline (a hydrolysis product of several herbicides, atrazine), copper, and lindane on *Chironomus riparius* and *Gammarus pulex*. Relative toxicity varied with chemical and exposure period up to 10 days exposure. 10 day LC₅₀ estimates for *C. riparius* were 4.2, 18.9, 0.2, and 0.013 mg/L, respectively. For *G. pulex*, the LC₅₀s were 5.0, 4.4, 0.033, and 0.007 mg/L. Other data of interest that were presented included a *C. tentans* LC₅₀ of 0.72 mg/L atrazine, and 0.16 mg/L 3,4-dichloroaniline for *D. magna*.

Hydra: Fu *et al.* (1994) compared the toxicities of industrial wastewaters to *Hydra attenuata* and fathead minnows. Of the 20 samples tested for acute toxicity, *Hydra* were more sensitive than fathead minnows to 16 samples (by factors of 1.1-5.5), equally sensitive to 2 samples, and less sensitive (by factors of ≤ 2.2) to two samples. The authors point out that *Hydra* were more sensitive to antimony than rainbow trout, fathead minnows, annelids, amphipods, and caddisflies.

Fish

One of the most compelling examples of declining productivity in the Estuary is the decrease in abundance of fish species. In the early 1900s, more than 25 canneries were operating in the Delta. However, overexploitation caused declines in many species and forced reduction and eventual elimination of commercial fishing for most species. While some species, such as the thicktail chub and Sacramento perch, disappeared in the early 1900s probably due to habitat alterations, declines for most of the remaining species have been most pronounced during the 1970s drought and since the subsequent drought in the mid-1980s. Strong year classes for some of these species, including Sacramento splittail, striped bass and longfin smelt, appear related to high Delta outflows. These data suggest that manipulation of flows during critical periods should improve year class strength. Alternatively, if toxic substances play a role in regulating year class strength, then the situation may be more complex than suggested by a simple relationship with flows, because flows play a role in diluting toxicants entering the system. Thus, toxicity would be a function not only of flow but also of application, degradation time, degree of toxicity, interactive effects, and effects of degradation products.

The effects would not necessarily have to be large in order to be significant. Small changes in density independent mortality rates can lead to declines and even extinctions over just a few decades (Jensen 1971). Alternatively, toxicants could indirectly affect fish by reducing numbers of preferred food organisms. In this case, reduced food abundance and associated reductions in growth rates can lead to appreciable increases in mortality rates.

The following section describes known effects of contaminants on fish inhabiting the San Francisco Bay Estuary. It also describes recent literature on effects which occur on the same species but in a different geographic region. Such information may be useful in examining the potential for similar effects in the Estuary.

Striped bass: Striped bass are probably the most important sportfishing resource in the Bay-Delta system (Moyle 1976). Adults spend summers in the Pacific Ocean and overwinter in the Delta. In the spring, they migrate to spawning grounds in the Sacramento river and lower San Joaquin River. The eggs and larvae drift with the currents to nursery areas in the Delta. Juvenile fish remain in the Estuary for approximately 3 years until they join the adult migration pattern. Thus, this species spends considerable time in the Estuary throughout all of its life history stages, making it vulnerable over a comparatively long period to potential exposures on the spawning grounds and in the Estuary itself. In addition, indirect effects on the population due to adverse impacts on food organisms could also occur.

Unfortunately, the numbers of adult striped bass have declined from approximately 2 million in 1967 to an estimated 574,000 in 1990 (Reynolds *et al.* 1993). This decline has been largely due to failure of recruitment (Stevens *et al.* 1985). In general, the cause of failed recruitment has been attributed to changes in patterns of water flow and exports in the Delta but the potential for impacts by toxic substances was also acknowledged (Stevens *et al.* 1985, Setzler-Hamilton *et al.* 1988).

Bailey *et al.* (1994) proposed that failure of recruitment of larval striped bass in the system was due to increased discharges of toxic pesticides associated with rice culture. Beginning in the mid-1970s, increased applications of these chemicals in the Sacramento Valley occurred as

culture practices changed and new cultivars were introduced to the farming community. The authors showed that a linear model that incorporated pesticides and river flows could explain nearly 90 percent of the variability of larval recruitment between 1973 and 1984, compared to the flow and export model which explained only 8 percent of larval recruitment during the same period.

The effect of rice-field discharges on larval recruitment is supported by several observations. The principle components analysis (Bailey *et al.* 1994a) suggested that the pesticides related to larval recruitment fell into two factors. One factor contained bufencarb while the other contained carbaryl, molinate, methyl parathion, carbofuran, and MCPA. This suggests that different modes of action or timing of application may be present. Bufencarb, since discontinued, is acutely toxic to striped bass early life stages at 0.1 µg/L, a concentration that easily could have been reached in the Sacramento River. The other chemicals are either herbicides or potent invertebrate toxicants which could be expected to affect other organisms in the food chain in downstream waters even if they did not directly affect striped bass (Bailey *et al.* 1994a; Finlayson *et al.* 1993; Menconi and Harrington 1992).

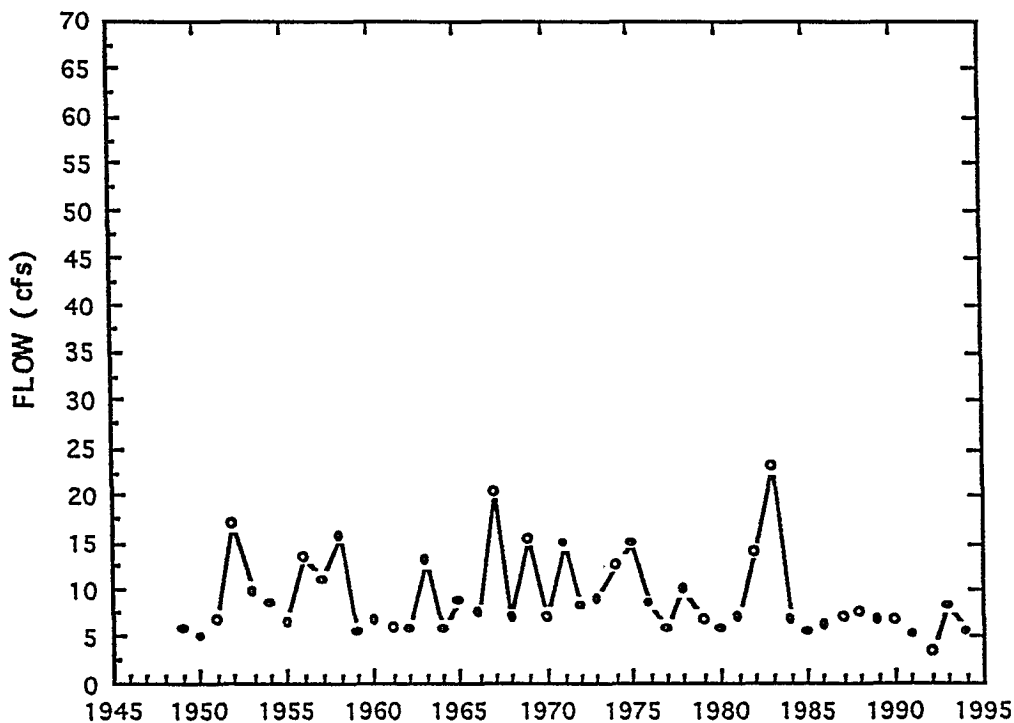
As evidence for adverse effects associated with rice-field discharges accumulated, longer holding times were required for selected pesticides prior to their release into the receiving water in order to provide additional time for dissipation. As the holding times increased, the pesticide model began to explain less of the variation in recruitment and the fit of the flow-export model improved (Bailey *et al.* 1994a), suggesting a reduction in pesticide impacts and a return to the importance of variables that historically controlled larval recruitment (Stevens *et al.* 1985).

As the holding times increased, toxicity associated with the samples also decreased, again suggesting a relationship between holding time and toxicity (Bailey *et al.* 1994b). A reduction in the frequency of liver lesions in field caught larval striped bass consistent with toxic exposure decreased to 15 percent in 1991 compared with a 25–30 percent rate of incidence in the two previous years (Bennett *et al.* in press). Interestingly, following the increased holding periods implemented for methyl parathion and molinate in 1991 and for carbofuran in 1992, the striped bass index has shown an appreciable improvement in spite of drought-like conditions in the Sacramento River. This is shown in the following table:

<u>Year</u>	<u>Index</u>
1988	4.6
1989	5.1
1990	4.3
1991	5.5
1992	10.6
1993	23.4
1994	10.6

While it might have been expected that the index would have quickly reached higher levels once the pesticides were effectively controlled and associated mortality rates reduced (Myers *et al.* 1995), this is not a likely scenario given the control that flow exerts on striped bass recruitment (Chadwick *et al.* 1977; Stevens *et al.* 1985). Low River flows, even in the absence of pesticides, effectively limit recruitment and prevent the development of strong year classes that would normally be associated with high flow years (Bailey *in prep.*).

Fig. 1. Average Sacramento River Flows at Grimes During May. Flow is given on the Y-axis in cfs X 1000 and year is given on the X-axis.



As Figure 1 suggests, flows in the Sacramento River during the spawning season since the mid-1980s have consistently averaged the lowest levels recorded. Moreover, the historical pattern of intermittent high flow years that could generate strong year classes has been altered as Sacramento River flows on the spawning grounds have been continuously maintained at low levels during the spawning season since 1983.

A comparison of Figure 1 and the 38-mm striped bass index data for the period 1988–1994 provides further evidence for the effectiveness of the pesticide control strategies. Between 1988 and 1991, the index ranged between 4.3 and 5.5, compared with a range of 10.6 to 23.4 between 1992 and 1994. Flows in 1992 and 1994 were lower than flows in the four previous years and flows in 1993 showed a small increase that corresponded to an increase in the index. Overall, these data are consistent with the removal of population limitation imposed by pesticide stress and also demonstrate the close relationship of the striped bass index and River flow. Note that other variables may influence recruitment besides flow, these include numbers of adult brood stock, water exports, and possible food limitations (Stevens *et al.* 1985).

Bennett *et al.* (in press) summarized the results of four years of field collections of larval striped bass in the Delta. Their principal conclusions, based on the examination of 500 larvae, were that the larvae did not exhibit evidence of starvation in any of the years but that the incidence of liver alterations typically associated with exposure to toxicants decreased to 15 percent in 1991 compared with 26–30 percent in the years 1988 to 1990. These authors commented on the futility of pursuing single-factor explanations for failure of recruitment, the potential interactions between toxic exposure, food limitations and predation, and the need for multi-disciplinary approaches to distinguish between anthropogenic intervention and estuarine processes that affect year class strength.

The difficulty of separating the effects of different variables on year class strength was also pointed out by Goodyear (1985) who investigated the causes of mortality of striped bass in Maryland. This investigator reported that it was not possible to distinguish between the relative contribution of mortality associated with contaminants and that resulting from fishing. Houde (1989) pointed out that very small differences in mortality rates and growth of eggs and larvae can have considerable effects on year class strength and that such small differences are virtually

impossible to detect with fisheries sampling techniques generally in use. In addition, Houde (1989) suggested that small changes in daily mortality rates within the first two months post hatch would probably have a much greater impact on year class strength than a decrease in the population's fecundity unless the drop in fecundity approached 80 percent.

Bailey and Doroshov (submitted) compared the survival of larvae from female striped bass collected from the Sacramento River. The female bass (n=8) ranged in weight from 4.0 to 14.2 kg. There was no relationship between female size and the survival of larvae reared in either fresh or salt water for 12 days following hatch. These data suggest that body burdens of contaminants in the adult fish were not high enough to produce adverse effects on survival of the offspring. However, other parameters that could be affected by elevated tissue levels of contaminants, including hatching success and growth of the larvae were not evaluated.

Setzler-Hamilton *et al.* (1988) compared recent trends in striped bass populations in the Chesapeake and San Francisco Bays. Populations in both bays exhibited sharp declines in numbers beginning in the mid-1970s, with young-of-the-year survival being the most obvious parameter affected. With respect to the San Francisco Bay population, body burdens of petroleum hydrocarbons, chlorinated hydrocarbons, and heavy metals were at levels of concern. Specifically, levels of monocyclic aromatic hydrocarbons (MAHs), alicyclic hexanes, and DDT in livers and ovaries of striped bass collected from the Sacramento and San Joaquin Rivers were correlated with egg resorption, abnormal egg maturation, and egg death. PCB concentrations in striped bass collected from San Francisco Bay were comparable to those found in striped bass from the Hudson River and, along with DDT (and metabolites) and toxaphene, at concentrations that would potentially affect the adult fish and their offspring. MAHs in livers and gonads of moribund fish collected from the Carquinez Straits averaged 2.4 mg/g (wet weight), approximately 50 times greater than levels found in viable pre-spawning fish. Survival of starved and fed striped bass larvae were inversely related to concentrations of chlorinated hydrocarbons, HCB, DDTs, PCBs, and chlordanes in the eggs. Stormwater and agricultural run-off appeared to be important sources of pollutants.

Other pesticides may also affect the survival of striped bass. Korn and Earnest (1974) evaluated the toxicity of 20 insecticides to juvenile striped bass under saline conditions. Among the most toxic chemicals was chlorpyrifos, with a 96-hour LC₅₀ of 0.53 µg/L, a

concentration that is exceeded in Delta waters. In addition, greater toxicity would likely be associated with earlier life history stages and in freshwater (Hall 1991).

Heath *et al.* (1992) examined the sublethal effects of rice pesticides methyl parathion, carbofuran, and molinate on larval striped bass. The authors concluded that methyl parathion and molinate reduced swimming performance and the effect persisted for at least 10 days after the 96-hour exposures. The authors also suggested that pesticide effects on food organisms could reduce food availability for larval striped bass and, therefore, indirectly limit larval swimming performance.

Bergerhouse (1993) evaluated the effect of elevated pH, ammonia and salt on the survival of larval hybrid striped bass. Up to six hours, survival was not affected by pH values of ≤ 9.4 . The threshold pH for mortality appeared to be between 8.7 and 9.2. The lethal threshold at 0.26 mg/L total ammonia nitrogen was between pH 8.38 and 8.75 for five day old larvae. These corresponded to unionized ammonia concentrations of 0.02–0.04 mg/L, respectively. The addition of 0.7% NaCl did not affect the survival of 2 and 4 day larvae at different pH levels but did significantly increase survival of 13 and 20 day larvae exposed to elevated pH. The higher salt concentration also reduced the joint effect of ammonia and high pH.

Hall (1991) reviewed the effects of water quality and contaminants on early life stages of striped bass. Findings of particular significance are reviewed here. 80 and 90 percent mortality were noted in larvae reared for 4 or 5 days in hardness of 34.6 and < 60 mg/L, respectively. Larval survival was maximized at salinities of 1–10 ppt. Suspended solids of 500–1000 mg/L increased larval mortalities while ≥ 200 mg/L reduced feeding efficiency compared with 75 mg/L. Cadmium, dieldrin and TBT were acutely toxic to larvae at approximately 1 μ g/L. Increased salinity appeared to reduce toxicity, particularly of mixtures.

Reardon and Harrell (1990) evaluated the acute toxicity of copper sulfate to striped bass fingerlings at varying salinities. These authors also cited Hughes (1971) who reported 0.1 mg/L copper sulfate to be LC_{50} to larval striped bass. For fingerlings, LC_{50} concentrations of copper sulfate were 2.68–7.88 mg/L over a range of salinities of 5 to 15 ppt. Tolerance increased as salinity increased.

Pinkney *et al.* (1990) investigated the effects of tri-n-butyl-tin (TBT) on the survival, growth, morphometry and RNA-DNA ratio of larval striped bass. Adverse effects on growth were seen at the lowest concentration tested, 0.067 µg/L, and 0.8 µg/L reduced survival.

Hall *et al.* (1988) investigated the effects of water quality in the Chesapeake Bay on striped bass prolarvae and yearlings using on-site and *in situ* studies. Survival of prolarvae was reduced in the Choptank River within 96 hour. Associated parameters that might have contributed to toxicity were: 36-48 mg/L hardness, 150 µg/L monomeric aluminum, 3 µg/L cadmium, and 40 µg/L copper. Histological evaluation of yearlings exposed to Choptank River water for nine days revealed alterations in gill and liver.

Kohlhorst (1973 and 1975) described the die-off striped bass and other species in the San Pablo-Suisun Bay area in 1971-1973. This die-off occurs annually between May and July, can involve thousands of fish, and is usually associated with the edge of saltwater intrusion. The co-occurrence of other species suggested a non-specific source of mortality. No evidence of elevated heavy metals were found. *Myxobacteria*, an opportunistic fish pathogen that frequently manifests itself when the host organism is stressed were found in a majority of the fish sampled. Based on the data obtained, Kohlhorst concluded that no specific cause of mortality could be identified and, therefore, no further surveillance was justified.

Cashman *et al.* (1992) compared chemical contaminants in moribund and healthy striped bass collected from the Estuary and Pacific Ocean. They concluded that the moribund fish were greatly contaminated by chemicals compared with healthy fish obtained from the Delta and Pacific ocean. The moribund fish were associated with annual die-offs of striped bass that most often are observed in the Carquinez Straits. These die-offs can include hundreds to thousands of fish and usually occur after spawning (Kohlhorst 1973 and 1975). Liver dysfunction was the most obvious aspect of the affected fish, but kidney and intestine were also involved. Livers of most of the moribund fish exhibited a mottled appearance. In addition to liver lesions, pathology of kidney, intestine, thyroid, and interrenal tissue were observed. Analytical measurements showed DDT levels in liver that ranged between 16 and 31 ng/g liver. Alicyclic hexanes were present at 0-10 ng/g liver and Arochlor 1260 was found at 440-760

ng/g liver. Dialkyl phthalates were detected in moribund fish livers at 10-20 times the concentrations found in the controls. Concentrations averaged 12-184 $\mu\text{g/g}$ liver for individual phthalates; cumulative phthalate concentrations were closer to 375 $\mu\text{g/g}$ liver. Liver concentrations of triazines and molinate were similar for control and moribund groups, but thiobencarb concentrations (1.2 $\mu\text{g/g}$ liver) averaged about 2 times higher than the controls (thiobencarb is metabolized in striped bass liver to a potent hepatotoxin). Aliphatic hydrocarbons were found at 0.2-2.7 $\mu\text{g/g}$ liver. These values were higher than in the controls; in addition, the chain length in the controls was limited to C16-22, whereas moribund fish contained chain lengths of C16-34. The authors proposed that the body burden of contaminants may have contributed to the die-off, perhaps as a multiple stressor interacting with osmotic stress.

Fabrizio *et al.* (1991) compared PCB concentrations in striped bass from different stocks on the Atlantic Coast. PCB concentrations were measured in edible filets (one side of skin on but w/o scales). PCB concentrations were variable, but fish from the Hudson river stocks had a higher probability of exceeding the 2 mg/kg limit for human consumption than did more southern stocks. This probability increased with age and size. Fish of ≥ 5 years old were most affected. At 610 mm minimum size (575 mm fork length) it was predicted that many harvestable fish would exceed tolerance limit set by Food and Drug Administration. (FDA reduced the tolerance limit from 5 to 2 mg PCB/ kg fish in 1984). The data suggested that the probability of exceeding the tolerance limit was 12 times greater in 7+ year old fish compared with 2-year old fish. Although highly variable, the relationship with size was also significant. Concentrations of PCBs in some fish exceeded 10 mg/kg and both sexes exhibited contamination. Uptake occurred through the water column and by ingestion of contaminated prey. Water-borne exposure was most significant for young fish and occurred relatively rapidly, with equilibrium reached within two weeks. Because mixed stocks overwinter in the Hudson River, all are exposed to waterborne PCBs. Alternative exposure occurred through food sources, primarily clupeids (herring), which are locally high in PCBs. The authors proposed that fishermen may need to target smaller fish to reduce the potential for harvesting fish that exceed the tolerance limit. However, the overall harvest rate would have to be reduced to compensate for higher mortality rates on younger fish.

Collectively, these data provide a basis for comparing body burdens and water-borne

concentrations of contaminants in the Estuary to those shown to be associated with adverse effects in other systems. They also suggest contributing factors to toxicity, particularly low salinity. Thus, early life history stages and adults during spawning are probably the most vulnerable. Multiple stressors are likely; striped bass are wide-ranging and sub-units of the population can vary dramatically in exposure and body burden of toxicants. A retrospective analysis suggests that the local striped bass decline may have been related to increased use and discharge of pesticides used on rice. Such effects would have been particularly apparent during low flow years when the dilution capacity of the River was minimal.

Flatfish: Starry flounder are another species that has recently declined in San Francisco Bay. Spies *et al.* (1988a; 1988b; 1990) evaluated the impact of organic contamination on reproductive success. These investigators found that fish collected from different sites in San Francisco Bay, particularly offshore of Berkeley and Oakland, exhibited reduced reproductive success compared with fish collected from other sites within San Francisco Bay and along the Pacific Coast. PCB concentrations in eggs were inversely related to successful embryological development. Mean liver lipid concentrations of PCBs were between 9.7 and 13.0 $\mu\text{g/g}$ in fish collected from Berkeley and Oakland, compared with 5 $\mu\text{g/g}$ in fish collected from Santa Cruz. Fish from other Bay sites, San Pablo Bay and Vallejo, also exhibited low (2–4 $\mu\text{g/g}$) concentrations of PCBs, suggesting that localized sources of contaminants were affecting the population. There were no relationships between fish weight and DDT or PCB concentrations in fish from any of the sites. One explanation offered by the authors is that induction of mixed function oxidase enzymes, particularly P450E, by chlorinated hydrocarbons, PAHs and other chemicals, may affect steroid metabolism, and consequently, the reproductive cycle, in exposed fish. This is supported by the inverse relationship with hepatic aryl hydrocarbon hydroxylase (AHH) concentrations and egg viability, fertilization and hatching success. Thus, there were site differences with respect to overall reproductive success, but PCBs were not the only factor that controlled the effects. Micronuclei in circulating erythrocytes were elevated in fish from all Bay sites compared to those from the Russian River. These were likely the result of exposure to PAHs and other mutagenic contaminants widely present in the Bay; PCBs and DDTs are not clastogenic.

Spies *et al.* (1993) compared the response of several biomarkers in speckled sanddabs

Citharichthys stigmaeus exposed to contaminated sediments collected from Castro Cove in San Francisco Bay. Increases were found in P-4501A (gill, liver, and kidney), particular in the gills. Hepatic 7-ethoxyresorufin O-deethylase (EROD) activity also increased up to 5-fold compared with the controls. Stress protein hsp 70 did not respond to exposure. Histopathological lesions were observed in gill tissues and were correlated with P-4501A in gill and with hepatic EROD activity. The amphipod *Eohaustorius estuarius* was also exposed to the sediment samples from this site. Amphipod mortality was highly correlated with hepatic EROD activity in *C. stigmaeus*. Thus, data from both species confirmed the deleterious effects of the sediments from this site.

Cyprinids: Cyprinids are widely distributed in the Delta and tributaries (Moyle 1976). Most of the species currently present have been introduced, but one native species, splittail, has been proposed for listing under the Endangered Species Act due to a relatively recent but sharp reduction in abundance. Saiki and Schmitt (1986) reported total DDT residues in samples from carp collected from the San Joaquin River that exceeded the National Academy of Sciences recommended safe level for the protection of fish-eating wildlife. These same samples exceeded the EPA estimated safe tissue concentration by factors of 8.7-14.7. Toxaphene tissue residues as high as 3.1 mg/kg were also reported. This tissue level exceeded the threshold for adverse effects by a factor of 6 (Eisler and Jacknow 1985).

Alam and Maughan (1993) evaluated the acute toxicity of diazinon and malathion to juvenile carp. The 96-hour LC₅₀s for diazinon were 3.43 and 4.97 mg/L. For malathion, values of 10.21 and 10.38 mg/L were obtained. Alam and Maughan (1992) reported juvenile carp LC₅₀ values of 0.3-1.0, 0.16-0.77, and 0.44-1.33 mg/L for copper, mercury and lead, respectively. Smaller fish were more sensitive. In general, these values are considerably higher than most values reported from the Bay, Delta, and tributaries.

Kaur *et al.* (1993) evaluated the effect of industrial effluents on the viability of carp eggs. Effluents from tannery, vegetable oil production, fertilizer production, and paper mill facilities were evaluated. NOEC were 0.0001, 0.0001, 0.01, and 0.1 percent effluent, respectively.

Kaur and Dhawan (1993) evaluated the sensitivity of carp eggs, 7-day larvae and 20-day fry to

carbaryl, carbofuran, malathion and phosphamidon in hard water. Concentrations of ≤ 50 , 10, 100, and 100,000 $\mu\text{g/L}$ did not affect hatchability. The greatest sensitivity occurred prior to gastrulation and closure of the blastopore. Larvae exhibited enlarged yolks and pericardial sacs, stunted tails, and vertebral column flexures; these are non-specific responses produced by a variety of toxicants, including metals, hydrocarbons, detergents and organochlorines. The authors concluded that "safe" values for the pesticides were 12, 3, 43, and 198 $\mu\text{g/L}$, under the conditions of exposure. Interestingly, early life stages of this species exhibited relatively high sensitivity to carbofuran. The "safe" concentrations is exceeded in the Delta on a fairly regular basis. Although difficult, similar studies would be worthwhile performing on eggs and larvae of other species.

Reddy *et al.* (1992) evaluated the effect of fenvalerate, a pyrethroid insecticide, on the survival and AChE system of carp. The 48-hour LC_{50} was 30 $\mu\text{g/L}$. At 10 $\mu\text{g/L}$, AChE was depressed and ACh increased relative to the controls. Of the tissues examined, the effect was greatest in the brain. The fish also exhibited sublethal effects and behavioral changes. Additionally, Reddy *et al.* (1991) reported that 10 $\mu\text{g/L}$ fenvalerate inhibited Mg- and Na-K ATPases in the gill, brain, liver and muscle tissues. For Mg-ATPase, the liver showed the greatest effect, followed by the muscle, brain, and gill. Conversely, Na-KATPase was most affected in the gill, followed by the brain, muscle, and liver. Effects were noted with exposure periods as short as 6 hours (the shortest period tested) and increased in magnitude as the exposure durations were increased to 48 hours.

Neskovic *et al.* (1993) examined the acute and subacute toxicity of atrazine, a triazine herbicide, to carp. The 96-hour acute LC_{50} was 18.8 mg/L. Significant changes in the activities of the alkaline phosphatase (serum, heart, liver, and kidney) and glutamic-pyruvic transaminase (liver and kidney) enzymes were found at 1.5 mg/L, the lowest concentration tested, after 14 days of exposure. Some small changes in gill histology were also noted at this concentration.

van der Weiden *et al.* (1992) evaluated the effect of sediment contaminated with polychlorodibenzo-p-dioxins (PCDDs), polychlorodibenzofurans (PCDFs), and polychlorobiphenyls (PCBs) on 7-ethoxyresorufin O-deethylase (EROD) activity and cytochrome P4501A content in carp. Both parameters were elevated following a 12-week

exposure and the effect persisted for at least 3 months.

Blevins (1991) described the results of an *in vitro* *Salmonella* assay using liver microsomal enzyme preparations prepared from carp collected from polluted and unpolluted habitats. When incubated with 2-aminofluorene, the number of revertants increased in relation to the degree of pollution the carp were exposed to. The data suggested that this assay may be useful for screening for polluted environments, particularly those contaminated with mutagenic or carcinogenic chemicals.

Ruiz and Lorente (1991) evaluated the seasonal accumulation of DDT and PCBs in carp muscle tissue from the Ebro Delta in Spain. Body burdens were found to increase in spring when channels opened for rice culture, which resuspended sediment particles containing bound contaminants. Later, another peak was found in tissue concentrations that corresponded to current applications of pesticides. Decreases in body burdens were found following reproduction and shedding of lipid-loaded gametes.

Kozaric *et al.* (1992) evaluated the effects of cadmium on hydrolase activities in liver and kidney of carp using histochemical methods. Non-specific esterase activity was inhibited in liver cells and kidney tubular cells. Acid and alkaline phosphatase activities were elevated in liver, but not in kidney. Exposure was 30 days at 240 µg/L. Whether these alterations would occur at lower concentrations was not established.

Tsuda *et al.* (1992) evaluated uptake and excretion of different pesticides in carp. There was rapid accumulation and depuration. The BCF for chlorpyrifos was 460 and equilibrium was reached in three days. The excretion rate was rapid, with a half-life of 34.7 hours. Captan exhibited a longer half-life (69.3 hours), but a BCF of only 100; equilibrium was reached within 24 hours.

Sunderam *et al.* (1992) exposed various fish species to endosulfan. Carp were the most sensitive, with a 96-hour LC₅₀ of 0.1 µg/L. For rainbow trout, the LC₅₀ was 0.7 µg/L (0.3 µg/L was reported elsewhere for trout). The LC₅₀ for mosquito fish was 3.1 µg/L.

Dyer *et al.* (1993) investigated the synthesis and accumulation of stress proteins in fathead minnows *Pimephales promelas* exposed to inorganic arsenic (sodium arsenite). The 96-hour LC₅₀ was found to be 9.9 mg As/L. The stress protein response was elicited within 2 hours in the gill at 25 mg/L arsenic. In the gill, synthesis of 20, 70, 72, and 74 kD proteins were significantly correlated with mortality. However, in striated muscle, only the 70 kD proteins were correlated with mortality. Gill tissue produced a greater variety of proteins and a greater response at lower concentrations than did muscle tissue.

Lindstrom-Seppa *et al.* (1994) described the uptake of 3,3',4,4'-tetrachlorobiphenyl (TCB) and induction of cytochrome P4501A in fathead minnows. High concentrations suppressed EROD activity. TCB was passed into eggs. Maintenance of CYP1A may last 2 weeks following induction. In female fish, estradiol may suppress CYP1A induction. Endothelial cell lining was an important source of CYP1A, with greater induction than in epithelial structures.

Hermanutz (1992) described malformations in fathead minnows reared in model ecosystems that contained waterborne selenium at concentrations of 10 and 30 µg/L. Thus, selenium was not only available in the water but also through dietary sources produced within the system. Fish were evaluated after approximately 1 year in the systems. Standing stocks were lower in the treated ecosystems than in the control systems and offspring exhibited a high incidence of externally visible malformations.

Changes in fathead minnow behavior following 24-hour exposures to pesticides were evaluated by de Peyster and Long (1993). 24-hour LC₅₀s for diquat and fenitrothion were 76.5 and 7.5 mg/L, respectively. Behavior was a more sensitive endpoint where changes were found at concentrations of 9.2 and 2.6 mg/L for diquat and fenitrothion, respectively. These concentrations were the lowest tested; behavioral effects may also have occurred at lower concentrations.

Hall and Oris (1991) evaluated the effect of anthracene on the reproduction of fathead minnows. Anthracene was accumulated by the fish and passed into the eggs. Larval deformities were observed as was reduced larval survival and reproductive output. The data

indicated that anthracene is toxic in absence of UV radiation. Females had higher BCFs than males and reproductive output was reduced by up to 52 percent. The NOEC was $< 6 \mu\text{g/L}$ in this study and $\leq 8.2 \mu\text{g/L}$ for daphnid reproduction (in absence of UV) as reported by Holst and Giesy (1989). The authors considered that reproductive effects could be related to interference with binding of hormones to receptor sites or interactions between MFO induction and hormone levels. Based on concentrations in eggs (wet weight) the NOEC fell between 3.75 and $8 \mu\text{g/g}$. A detailed discussion of interactions between MFOs and potential reproductive effects was also presented.

Weber *et al.* (1991) evaluated the effects of a 4-week exposure to waterborne lead (0.5 and 1.0 mg/L) on feeding abilities and neurotransmitter levels in juvenile fathead minnows. Lead-exposed fish exhibited reduced ability to feed on live prey. Brain levels of serotonin and norepinephrine were increased following exposure, but there was no change in dopamine concentration. These concentrations are quite high compared with environmental levels, but there may be similar effects at lower concentrations as this study did not establish a NOEC.

Lien and McKim (1993) evaluated the uptake of 2,2',5,5'-tetrachlorobiphenyl in fathead minnows. The authors found that uptake across the skin was similar to that across the gills and attributed this to the relatively large surface to volume ratio and the comparatively small diffusion distance compared with larger fish.

Welsh *et al.* (1993) investigated the effects of dissolved organic carbon (DOC) and pH on the toxicity of copper to larval fathead minnows. Toxicity was inversely related to DOC and pH. The LC_{50} s ranged from 2 (pH 5.6, DOC 0.2 mg/L) to $182 \mu\text{g/L}$ (pH 6.9, DOC 15.6 mg/L). A predictive equation that incorporated DOC and pH explained 93 percent of the variation in toxicity within a pH range of 5.4 - 7.3 and DOCs of 0.2 - 16 mg/L. The toxicity of zinc was also reduced by the formation of organic complexes.

Hickie *et al.* (1993) evaluated the toxicity of trace metals to larval rainbow trout and fathead minnows. Below pH 4.9, aluminum was the dominant toxic cation while copper was predominant at pH 5.8. Rainbow trout were less sensitive to low pH and metal ions than the fathead minnows.

Hartwell *et al.* (1989) compared toxicity and avoidance response to five metals with golden shiner. 96-hour LC₅₀s for chromium, copper and arsenic were 55, 84.6 and 12.5 mg/L; shiners exhibited avoidance response at 2 orders of magnitude lower concentrations. No avoidance response was observed with cadmium (up to 68 µg/L) and selenium (up to 3.5 mg/L). The LC₅₀s for these metals were 2.8 and 11.2 mg/L, respectively, at a water hardness of 72 mg/L.

Chiasson (1993) measured avoidance responses in golden shiners to suspended sediment concentrations of 15, 75 and 150 JTU. Responses were noted at 75 and 150 JTU.

Salmonids: Salmonids in the Delta are generally comprised of different races of Chinook salmon and steelhead (Moyle 1976). Central Valley salmon stocks have declined from approximately 1 million returning adults in the early 1900s to around 100,000 adults currently (Reynolds *et al.* 1993). Numerically, fall-run Sacramento River Chinook are the most abundant salmonid in the Estuary. Other races of Chinook salmon, including the late-fall, spring and winter Sacramento River fish as well as fish entering the San Joaquin drainage probably make up less than 20 percent of the remaining adult fish. The number of steelhead trout has also been reduced to just a few thousand returning adults (CDF&G 1993). Salmonids primarily use the Estuary as a migratory pathway to the ocean as smolts, and back to their natal streams as adults. Thus, these fish are potentially exposed to contaminants in their nursery areas and during their migrations. For example, fish migrating in and out of Butte Creek must pass through either Butte Slough or Sacramento Slough, both of which receive large quantities of agricultural discharge water, primarily from rice (Reynolds *et al.*, 1993). In addition, indirect effects could occur if the outmigrating smolts depended on invertebrates for food and such food sources were reduced by exposure to contaminants. The potential for adverse effects may be exacerbated for steelhead since the young spend considerably more time in fresh and brackish water environments than do Chinook salmon. Unfortunately, there is very little information on the effects of contaminants in the Estuary on salmonids. Therefore, most of the following discussion reflects studies conducted elsewhere.

Servizi and Gordon (1990) evaluated toxic interactions between ammonia and suspended sediment with juvenile chinook salmon. The LC₅₀ of suspended sediment was 31 mg/L and

the LC₅₀ for ammonia was 0.45 mg/L (as un-ionized ammonia). Joint toxicity was slightly less than additive.

Short and Thrower (1987) investigated the toxicity of TBT to juvenile chinook salmon. The 96-hour LC₅₀ was 1.5 µg/L. TBT concentrations in the brain, liver and muscle were 200 – 4300 times higher than the concentration in water. The linear relationship between exposure time and mortality suggested that longer exposures would result in additional mortalities at lower concentrations.

Pinkney *et al.* (1990) found that 0.2 µg/L TBT reduced growth in rainbow trout fry and 0.09 µg/L reduced growth in silversides. Both values were lowest concentrations tested.

Mitchell *et al.* (1987) investigated the acute toxicity of the herbicides Rodeo and Roundup to rainbow trout, chinook, and coho salmon. For Roundup, based on total formulated product, the 96-hour LC₅₀s ranged between 15 and 22 mg/L. Based on glyphosate, the active ingredient, the LC₅₀s ranged from 7.4 to 12 mg/L. Rodeo was less toxic; based on total formulation, the LC₅₀s ranged between 680 and 1440 mg/L. Based on glyphosate, the LC₅₀s were 130 to 290 mg/L. Coho salmon smolts challenged with seawater were not affected by up to 2.78 mg/L Roundup, based on total formulation (Chapman).

Hamilton and Buhl (1990) investigated the effects of arsenate, arsenite, cadmium, copper, mercury, silver, vanadium, and zinc on chinook salmon fry. These metals are associated with discharge from the San Luis Drain that collects irrigation waters from the west side of the San Joaquin drainage. In terms of toxicity, cadmium and copper > mercury > zinc > vanadium > arsenite > arsenate > chromium (no definitive tests were completed with silver due to precipitation). By comparing toxicity to actual concentrations found in the Drain, Cd, Cu, Hg, and Zn were estimated to be of concern in fresh or brackish receiving waters. LC₅₀s for the first three metals ranged from 17–101 µg/L, whereas the LC₅₀ was 1.3–2.9 mg/L for zinc. Toxicity continued to increase over the 96-hour exposure period, particularly for cadmium, suggesting that longer exposure would be associated with increased effects. In most cases, brackish water appeared to reduce toxicity. Mixtures of the metals exhibited approximately additive toxicity.

Hamilton *et al.* (1990) evaluated the effect of dietary selenium on chinook salmon. Survival was reduced in fish fed ≥ 9.6 $\mu\text{g/g}$ selenium and growth was reduced in fish receiving ≥ 5.3 $\mu\text{g/g}$ selenium. The selenium was introduced by incorporating mosquito fish, obtained from San Luis Drain, that contained high selenium levels into the fish meal component of the diet. Selenium was not concentrated in the salmon to levels greater than in the diet.

Ictalurids: Ictalurids, primarily channel and white catfish and brown bullhead, are introduced species that are widely distributed throughout the Delta, although the numbers appear to be declining. Lin *et al.* (1994) looked for metabolites of polycyclic aromatic hydrocarbons (PAHs) in the bile of brown bullhead *Ameiurus nebulosus* collected from four tributaries to Lake Erie. Concentrations of PAH metabolites in the bile of fish from sites with contaminated sediments were 5-20 times greater than those from sites with uncontaminated sediments.

Murdoch and Hebert (1994) measured mitochondrial DNA diversity in brown bullhead from sites in the Great Lakes having sediments contaminated with heavy metals, PAHs, PCBs, chlorinated pesticides, and petroleum hydrocarbons. Their results demonstrated considerable differences in mDNA between sites, with a consistent reduction in haplotype diversity at contaminated sites compared with fish sampled at reference sites. The authors concluded that the decreased diversity was associated with population bottlenecks, in this case severe selection associated with environmental degradation, i.e., pollution. They also pointed out the advantages of brown bullheads for this type of research; they are sensitive to contaminants frequently found in sediments and tend to be representative of local conditions because they do not undergo extensive migrations.

Steward *et al.* (1990) investigated the metabolic fate of benzo[a]pyrene (BP) in brown bullhead. Most of the BP was found in the bile, liver, and gut, with significant quantities also associated with the spleen, gonads, and muscle. The hepato-biliary system was the major route of excretion. Metabolism produced the highly genotoxic BP-7,8-diol and other bioactive metabolites. The presence of the parent compound and active intermediates in the muscle is of concern to those who consume contaminated fish.

Hasspieler *et al.* (1994) compared glutathione (GSH) response against xenobiotics in channel catfish and brown bullhead. Brown bullhead mounted less of a response and maintained lower levels of hepatic total glutathione and reduced glutathione than channel catfish. This is consistent with brown bullhead expression of neoplasms in contaminated systems compared with channel catfish which rarely express pollutant-mediated neoplasia. Thus, brown bullhead would appear to be more sensitive to GSH arylators and oxidants. Reduced glutathione protects against oxidants as an antioxidant defense and is a substrate for conjugation reactions.

Gallagher and DiGiulio (1989) evaluated the effects of complex waste mixtures on hepatic monooxygenase activity in brown bullhead. In spite of lip and jaw lesions and liver damage, measures of MFO activity (cytochrome p450, EROD, etc.) were not good indicators of fish from the contaminated site. The authors pointed out that MFOs may respond well to specific chemicals (PAHs and PCBs), but their response to complex mixtures is not well characterized. Furthermore, the presence of selected metals may suppress enzyme activity.

Gallagher and DiGiulio (1992) investigated the role of fish gills in glutathione-mediated detoxification of the fungicide chlorothalonil. Gills were found to be an important component in metabolism and detoxification of this chemical (the chemical undergoes direct conjugation with GSH without prior oxidation with cytochrome P-450). GSH levels increased within 72 hours of exposure and were maintained through the metabolism of cysteine. Davies (in Gallagher and DiGiulio 1992) showed that chlorothalonil accumulates 1000 fold in rainbow trout gills and reduces lamellar diffusion. Species that have high capacity to detoxify electrophilic contaminants may have an advantage in environments that contain such contaminants.

Kim *et al.* (1989) compared the pathology of brown bullhead from contaminated and relatively clean sections of the Hudson River. The study section of river is contaminated with PCBs and, to a much lesser extent, with polychlorinated dibenzofurans and polychlorinated dibenzodioxins. The condition factor of fish from the contaminated site was lower than fish from the control site, but was not different between fish of different sexes from the same site. Muscle levels of PCBs in fish from the contaminated site averaged 38 µg/g, compared with 0.61 µg/g in fish from the control site. The sex ratio (M/F) was 0.25 at the contaminated site

vs 1.2 at the control site. The incidence of gross abnormalities were similar in fish from both sites, but histopathologic alterations in spleen, kidney, and liver were considered definitive markers of fish from the contaminated site. Bile duct hyperplasia was considered the most significant finding. Hemosiderin in liver, spleen, and kidneys suggested the breakdown of red blood cells, and metals such as cadmium, lead and mercury were considered likely causative agents.

Baumann *et al.* (1991) compared tumor frequencies in brown bullhead with concentrations of sediment contaminants in tributaries of the Great Lakes. Tumor frequency appeared related to polynuclear aromatic hydrocarbons (PAHs), rather than polychlorinated aromatic hydrocarbons. Hepatosomatic indices were also higher in association with PAHs. PAHs in the sediment from the contaminated site totaled 10.8 $\mu\text{g/g}$ dry weight. Body burdens of PAHs in fish from contaminated site were 220 ng/g wet weight.

Pangrekar and Sikka (1992) described the xenobiotic metabolizing enzymes in the liver and kidney of brown bullhead exposed to the PAH 3-methylcholanthrene. After 7 days, treated fish showed increased activity of aryl hydrocarbon hydroxylase in liver and kidney, with little effect on epoxide hydrase or glutathione-S-transferase. This may be of concern because the secondary enzymes that detoxify the oxidative products were not induced in the same time course as the oxidizing enzymes, potentially leaving increased levels of arene oxides or epoxides available to interact with cellular components. Microsomal preparations from liver and kidney treated with benz(a)pyrene showed that liver microsomes converted a greater proportion to BP -quinones than kidney preparations. The quinones are known to cause DNA damage and may be related to the susceptibility of brown bullhead to liver tumors. Interspecific differences in formation of quinones was noted and may be a reason for differences in species susceptibilities.

Gallagher *et al.* (1992) investigated the acute toxicity of the fungicide chlorothalonil to channel catfish. Toxicity was increased 3X (120 vs 40 $\mu\text{g/L}$) following depletion of liver and gill glutathione (GSH). Exposure to chlorothalonil induced GSH levels in liver and gill. Data indicated that exposure to multiple toxicants may exacerbate toxicity as one or more of the chemicals deplete tissue GSH levels.

Sikka *et al.* (1990) compared the metabolism of benzo[a]pyrene (BP), a polycyclic aromatic hydrocarbon, in hepatic microsomes from brown bullhead and carp. BP was metabolized over 10 times faster in carp microsomes than in brown bullhead microsomes. Similar metabolic products were obtained, but carp produced a much greater proportion of benzo-ring dihydrodiols compared with brown bullhead, which produced largely BP-phenols and BP-quinones. These results may explain the greater propensity of brown bullhead to form epidermal and hepatic tumors.

Plumb and Areechon (1990) examined the effect of a 30-day exposure to malathion on the immune response of channel catfish challenged with the pathogen *E. ictaluri*. 1.74 mg/L malathion reduced the antibody response by 85 percent compared with the control, and 0.5 mg/L reduced the response by 20 percent compared with the control. Deformities (80 and 10 percent, respectively) and behavioral changes were also noted at both pesticide concentrations.

Mosquitofish: Mosquito fish *Gambusia* sp. are a widely distributed live-bearing species introduced to California for mosquito control (Moyle 1976). They are tolerant of a wide range of water quality conditions, making them useful for vector control in standing and flowing waters as well as ephemeral pools. Lee *et al.* (1992) evaluated the effect of acute inorganic mercury exposure on populations of mosquitofish. There was a maternal effect in that groups of fish that shared a common mother exhibited similar sensitivities to mercury. This implies a heritable genetic component to sensitivity.

Chagnon and Guttman (1989) evaluated the effect of copper and cadmium on the survival of populations of mosquitofish containing different allozyme genotypes. For both metals, differences in survival were associated with different genotypes. The authors noted that correlations between heavy metal stress and allelic and genotypic frequencies at the phosphoglucosmutase (PGM) and/or the glucose phosphate isomerase (GPI) loci have been generally noted in marine and freshwater invertebrates and fish. Strittholt *et al.* (1988) suggested that the current lack of allozyme variability in yellow perch in Lake Erie was due to selection from heavy metal pollution.

Heagler *et al.* (1993) also investigated the effect of mercury exposure on allozyme genotypes

in mosquitofish. One of the nine loci investigated, GPI, was correlated with time to death in the laboratory study. A follow-up investigation compared fish from mercury-contaminated and control sites. The fish from the contaminated site exhibited significantly lower frequency of one of the GPI alleles than did fish from the uncontaminated site.

In follow-up work, Kramer and Newman (1994) compared the effect of mercury on the gluconeogenic properties of preparations of two different GPI allozymes. The results suggested that the allozyme generally associated with increased sensitivity to mercury (and arsenic), *Gpi-2³⁸/38*, was not differentially inhibited by mercury, suggesting that the associated allele was a marker closely related to a gene(s) that confers susceptibility to Hg toxicity.

Tietze *et al.* (1991) evaluated the toxicity of chemicals used in control of mosquitos to mosquito fish. The most toxic material was the pyrethroid insecticide resmethrin, with a 24-hour LC₅₀ of 7 µg/L.

Centrarchids: Centrarchids are widely distributed in the Delta and tributaries. Current populations are composed primarily of introduced species which have eliminated the only native centrarchid, the Sacramento perch, from most of its former range (Moyle 1976). McCloskey and Oris (1991) investigated the toxicity of anthracene, a model polycyclic aromatic hydrocarbon, to bluegill. Potential interactions with toxicity and temperature and dissolved oxygen levels were observed. Toxicity was increased in the presence of UV light, and was not expressed up to 35 µg/L in the absence of UV light. In the presence of UV light, 96-hour LC₅₀ concentrations ranged from 1.3 – 8.3 µg/L.

Atherinids: The primary species of atherinid in the Delta is the introduced silverside *Menidia beryllina*. Two native atherinids, topsmelt and jacksmelt, are also found in the estuary, but generally in the more saline waters of San Francisco Bay (Moyle 1976). Middaugh *et al.* (1991) examined the effect of water contaminated with PAHs on toxicity and teratogenicity in silversides. Exposure to contaminated sediments near discharge site resulted in rapid increase of liver cytochrome P-450-IA1 in juvenile fish. Liver and skin lesions were present in another species, spot, collected from the discharge site. Effects were observed in

Menidia embryos exposed for ten days until hatching at concentrations of 0.28–2.1 mg/L, while no effects were observed at concentrations of 0.028–0.15 mg/L. Ultrafiltration reduced the concentration of PAHs by almost a factor of 100. In general, PAHs' rate of decomposition is almost constant, while anthropogenic inputs, such as oil products and spills, burning, and oil refining, have increased. Eagle Harbor (Washington) sediments contain up to 6.5 g/kg dry weight PAHs in sediment and exposure has produced liver lesions in fish. Liver lesions are also present in fish (*Fundulus*) in the Elizabeth River (Virginia) which averages 2.2 g PAH/kg dry sediment.

Hemmer *et al.* (1992) compared the sensitivity of larval topsmelt and silversides to a variety of chemicals using static 96-hour tests and 7–33 day old fish. LC₅₀s were within a factor of 2 for most chemicals but varied up to a factor of 6.7. Seven-day old fish were approximately 20 percent more sensitive than 28 day old fish. In comparisons with other species, bluegill were generally more sensitive (average 3X), trout next (average 2X), and fathead minnows quite a bit less sensitive (from 23X up to 63X). Reproducibility within laboratories for these tests was 1.4–2, and reproducibility between labs was within a factor of 4.4. The authors also noted that fathead minnows were particularly insensitive to OPs.

Other fish species and findings of interest: Noga *et al.* (1991) described dermatological disease in fish from the Tar-Pamlico Estuary in North Carolina. Ulcerative mycosis affected a variety of species including striped bass and flounder. Only one tumor was found. While the causes were not determined, the mycosis appeared to primarily affect fish found in intermediate salinities, rather than high salinities or in freshwater.

Vittozzi and De Angelis (1991) reviewed acute toxicity data on fish. Fish species included rainbow trout, fathead minnow, bluegill, carp, medaka (*Oryzias latipes*) and zebrafish (*Brachydanio rerio*). 200 chemicals were evaluated, of which approximately ten percent were phosphoesters, including diazinon, chlorpyrifos, and malathion. Carbamates were also represented. No relationship between n-octanol water partition coefficient and toxicity was found. Evidence for species-dependent toxicity was found, and differences between species varied by factors of 10 to 300. Organophosphorous chemicals (OP insecticides) generally accounted for most of the species selective toxicity observed in the data set. Fathead minnows were the most resistant species in virtually all comparisons. OPs were generally 10–300 times

more toxic to bluegill than to fathead minnows. OPs also exhibited greater toxicity to trout than to fathead minnows, and the trout were up to 160 times more sensitive than fathead minnows. Differences in sensitivity may be due to differences in sensitivity of cholinergic system and/or development of detoxification systems. In general, since approximately 4 of 100 chemicals shows species-dependent toxicity, use of one species to assess effects is not adequate. However, this frequency is much higher for organophosphorous chemicals. Therefore, one could consider the use of safety factors. In this case, a safety factor of 100 applied to fathead minnow data would include all but the three most selective OP chemicals.

Thybaud (1990) investigated differences in toxicity between lindane, a chlorinated hydrocarbon, and deltamethrin, a new generation pyrethroid. Lindane exhibited high bioaccumulation but lower toxicity. Deltamethrin was rapidly metabolized. Deltamethrin approximately 100 to 1000 times more toxic to *Rana* tadpoles and mosquito fish than lindane.

Clearance and uptake rates and total amount of contaminant accumulated may vary with changes in salinity. With higher salinities, clearance rates of pentachlorophenol (PCP) increased and uptake rates decreased in the killifish (*Oryzias latipes*). Freshwater-acclimated fish accumulated more PCP than saltwater fish (Tachikawa and Sawamura 1994).

Birds

Double-crested cormorant: Cormorants are present in the Estuary where they occupy a similar niche high in the food web. Therefore, they are a good indicator species to evaluate trophic effects of contaminants. By determining contaminated components of the forage base, insights can be gained regarding sediment and/or water column contaminants of concern.

Jones *et al.* (1994) evaluated the biomagnification of PCBs and TCDD-equivalents in eggs and chicks of the double-crested cormorant *Phalacrocorax auritus* at different sites in the Great Lakes. Toxic concentrations of these materials result in induction of mixed function oxidases, depletion of hepatic retinoids and vitamin A, porphyria, edema and wasting syndrome. Similar effects were also seen in salmonid fishes and mink in the Great Lakes. The biomagnification factor from forage fish to cormorant eggs was 31.3. Concentrations in the chicks decreased

immediately following hatching, then increased in proportion to the mass of fish consumed. Once the chicks initiated thermoregulation, the rate of accumulation increased. Weathering actually increased the proportion of more toxic PCB congeners compared with the original Arachlor mixture. Concentrations in chicks were more closely associated with local conditions than concentrations in eggs, since foraging for young usually occurred relatively close to the nesting site. Adults tended to mix and forage widely when not feeding young.

Davis *et al.* (in preparation) measured EROD activity in double crested cormorant embryos as an indicator of accumulation of dioxin-like compounds at the top of the aquatic food web of San Francisco Bay. In both 1993 and 1994, median activity in samples from the 2 locations in San Francisco Bay (at the Richmond Bridge and near the San Mateo Bridge) was elevated 4- to 8-fold over a coastal control location and these differences were statistically significant ($p < .05$). In experimental injections of double-crested cormorant eggs with TCDD, Sanderson and Bellward (submitted) found that a dose (3 ppb) causing a 5-fold increase in EROD coincided with the lowest dose at which mortality and subcutaneous edema (characteristic consequences of exposure to dioxin-like compounds), began to appear in the embryos. Therefore, the 4- to 8-fold increase in EROD in double-crested cormorant embryos from San Francisco Bay suggests that they are also exposed to a concentration at the threshold for toxic effects in this species. The elevated microsomal EROD activities observed in colonies in San Francisco Bay is consistent with many other datasets indicating enrichment of this ecosystem with polychlorinated biphenyls (PCBs). Morphological and histological effects of exposure to dioxin-like compounds and other toxicants are also being evaluated in these embryos.

Black-crowned night herons: Pollutant accumulation and effects have been studied relatively extensively in black-crowned night-herons *Nycticorax nycticorax* in San Francisco Bay. In 1982, Ohlendorf *et al.* (1988) found that 5 of 47 (10.6%) night-heron eggs collected at Bair Island in the South Bay exceeded 8 ppm DDE, a concentration associated with impaired reproduction in this species. Eggshell thickness in these eggs was negatively correlated with DDE concentrations. Further studies at Bair Island in 1983 (Hoffman *et al.* 1986) showed that total PCB concentrations in night-heron eggs were negatively correlated with embryo weights. Other signs of impaired growth in these embryos included reduced crown-rump lengths and femur lengths. Other species nesting at Bair Island during this period, including

Caspian terns (*Sterna caspia*), Forster's terns (*Sterna forsteri*), and snowy egrets (*Egretta thula*), also exhibited concentrations of organochlorines similar to those observed in night-herons. Mercury and DDE concentrations in Caspian tern eggs were higher than those in the other species.

Using samples collected in 1982 and 1983, Ohlendorf and Marois (1990) measured selenium, DDE, chlordanes, and PCBs in black-crowned night heron eggs from Bair Island, Mallard Slough, and two locations in the South Bay. Mean shell thickness of these eggs was significantly lower (8-13% lower) than in museum specimens collected before the widespread use of DDT and was negatively correlated with DDE concentration. DDE concentrations in some of these eggs were higher than 8 ppm, the level associated with reduced reproductive success of night-herons.

Hothorn *et al.* (in press) conducted further studies on pollution and reproduction in black-crowned night-herons and snowy egrets in 1989-1991. Mercury, selenium, and organochlorines were analyzed in eggs and reproductive success was monitored in several locations on San Francisco Bay. Although many broken shells and 2 incidences of teratogenesis were observed, concentrations of contaminants were generally lower than threshold levels for such effects. No clear spatial or temporal trends emerged from these analyses.

Diving ducks: San Francisco Bay is an important wintering area for waterfowl. Trace element accumulation has been studied extensively in two diving duck species, greater scaup (*Aythya marila*) and surf scoter (*Melanitta perspicillata*). Ohlendorf *et al.* (1986a) found that mean concentrations of selenium, silver, copper, mercury, zinc, and cadmium were higher in these species in South San Francisco Bay than in Chesapeake Bay. Mean selenium concentrations in scoters (34.4 ppm, dry weight) were similar to those in dabbling ducks at Kesterson reservoir where severe impairment of reproduction occurred (Ohlendorf *et al.* 1986b). Mercury in scoter and scaup was also present at concentrations associated with impaired reproduction and altered behavior in experimental studies of mallards (Heinz 1979).

Ohlendorf *et al.* (1990) conducted further studies of trace element and organochlorine contamination in surf scoters in 1985. Of the six Bay locations studied, mean selenium

concentrations were highest in San Pablo Bay and were similar to those found in American coots at Kesterson Reservoir that died of selenium toxicosis. Scoter body weights were negatively correlated with mercury concentrations.

Selenium concentrations in diving ducks in the Estuary were also measured in the Selenium Verification Study (White *et al.* 1987, 1988, 1989). Diving ducks (scaup and scoters) wintering on Suisun and San Pablo Bays accumulated higher selenium concentrations than their counterparts in Humboldt Bay, located on the California coast near the Oregon border. From 1986 through 1988, selenium concentrations in this portion of the Estuary increased each year. By 1988 concentrations of selenium in surf scoters from Suisun Bay reached a mean of 58 ppm in liver, more than 20 times higher than scoters from Humboldt Bay. In San Pablo Bay, concentrations in scoters averaged 36 ppm. Based on findings from this study, the Department of Health Services issued an advisory recommending limited consumption of scaup and scoters from Suisun Bay in 1986. Toxic effects have not yet been observed on diving ducks due to selenium, but because these species breed in Canada and Alaska, examination of possible effects on reproduction, the most sensitive lifestage to selenium toxicosis, is highly problematic.

The ethoxyresorufin-o-deethylase (EROD) assay is a sensitive biomarker of exposure to dioxin-like chemicals -- including dioxins, polychlorinated biphenyls (PCBs), dibenzofurans, and others -- in birds and other animals. Melancon *et al.* (1992) measured EROD activity in greater scaup, surf scoter, and ruddy ducks from Suisun Bay. EROD activities in scaup and ruddy duck livers were approximately 2- and 3-fold higher, respectively, than in controls collected from a coastal site in Tomales Bay, thus indicating accumulation of dioxin-like compounds. EROD activity in scoter liver was not elevated in Suisun Bay, possibly suggesting dietary differences between the species.

California clapper rail : Lonzarich *et al.* (1992) measured concentrations of mercury, selenium, PCBs, and organochlorine pesticides in eggs of the endangered California clapper rail (*Rallus longirostris obsoletus*) collected in 1975, 1986, and 1987. Mercury concentrations in these eggs were higher than at a reference location and comparable to concentrations associated with reproductive effects in other species. Concentrations of

selenium in some individuals approached values associated with embryotoxicity in other rail species. Selenium concentrations were highest in a marsh adjacent to the Chevron refinery in San Pablo Bay. Data were not available from the 1975 samples on the concentrations of trace elements, so long term trends were not characterized. Organochlorine concentrations were relatively low and decreased in the 1986 and 1987 samples relative to the 1975 samples.

California black rail: Evens *et al.* (1991) reviewed the status of the California black rail. The bulk of the population was confined to the northern marshlands of San Francisco Bay. The populations are undergoing a decline, presumably due to habitat loss or degradation. The effects of contaminants are not known, but have affected other bird species in the Estuary that occupy similar trophic levels.

Willet: Custer and Mitchell (1991) evaluated contaminants in willets (*Catotrophorus semipalmatus*) collected at outlets of two agricultural drains in Texas. Elevated arsenic levels in liver were noted, but concentrations (up to 15 ppm dry weight) were less than associated with acute toxicity. Selenium concentrations were not elevated over background. Mercury concentrations (2-17 ppm) were elevated, but were generally less than associated with mortality. However, the mercury concentrations were high enough to produce reproductive effects. Cholinesterase (ChE) in brain tissue did not indicate recent exposure to OPs. However, ChE depression was observed in the past and could have been associated with recent application of OP or carbamate insecticides. Only arsenic was elevated in the agricultural drains. The authors indicated that body burdens of 12-68 ppm DDE are dangerous to birds.

Blackbirds: Blackbirds are most often affected by pesticide applications in roosting, nesting and/or foraging areas. Meyers *et al.* (1992) evaluated the toxicity of chlorpyrifos and dimethoate to red-wing blackbirds (*Agelaius phoeniceus*) and starlings (*Sturnus vulgaris*). For dimethoate, the reported LC₅₀ values for adult starlings and blackbirds were 32 and 6.6 mg/kg, respectively. For chlorpyrifos, the values were 5.0 and 13.0 mg/kg, respectively. Nestlings responded differently. A single dose (oral) of 2 mg/Kg chlorpyrifos reduced the survival of blackbird nestlings by approximately 50 percent over a 10 day period, but did not affect survival of starling nestlings. In contrast, a single dose of 50 mg/kg dimethoate did not affect the survival of blackbird nestlings, but reduced the survival of starling nestlings by 56

percent. Growth was not affected in birds that survived exposure.

Bald eagle: Bald eagles occupy high trophic levels and so may be contaminated by xenobiotics that accumulate in the food chain to harmful levels. They may also be adversely affected by ingesting lead fragments in dead or wounded waterfowl (Langelier et al 1991 and Gill and Langelier 1994) or by accidental pesticide poisoning (Bowes *et al.* 1992, Colborn 1991). Pesticides associated with eagle mortalities include dieldrin, endrin, DDE, DDT, and carbofuran. Although bald eagles are generally present in the Bay/Delta system only on a seasonal basis, the following information is presented because it provides a fairly complete picture of contaminant effects which is lacking for many species in similar trophic levels. Thus, monitoring other key indicator species, such as terns, gulls, grebes, cormorants, and so on, should provide a valuable basis upon which to compare trophic effects with those identified in the Great Lakes and elsewhere.

Data from bald eagle populations in the Great Lakes suggests that accumulation of toxic chemicals through the food chain has reduced reproductive success in several populations. The chemicals of major concern include DDT, DDE, PCBs, dioxins, and furans (Colborn 1991). The problem is exacerbated because the eagles not only feed on contaminated fish, but also on birds that feed on the fish, thus effectively increasing the biomagnification. Other birds feeding on the same types of food are also experiencing reproductive failures, including Caspian, Forster's, and common terns, osprey, double-crested cormorant, and herring gull. Since the eagles are transient to the Bay/Delta, looking at some of these other fish-eating bird species that are residents would be appropriate. Mink and otter, semi-aquatic mammals resident in the Bay/Delta and tributaries, were also indicated as species showing reproductive failure and population declines consistent with eagles in the Great Lakes system.

Grubb *et al.* (1990) reviewed the relationship between eggshell thinning and contaminant levels in bald eagles in Arizona. Eggshells were still thinner than from pre-DDT era, but productivity was improving. All eggs analyzed included detectable levels of mercury, DDE, and PCBs. Mercury was below levels known to cause effects. Concentrations of contaminants (DDE and PCBs) decreased in eggs between 1977 and 1982. Overall, DDE levels of 1-2 ppm wet weight in eggs did not appear to affect reproductive success and neither did PCB levels of 0.4-0.9 ppm. Local populations varied appreciably in their tissue

concentrations.

Anthony *et al.* (1993) described environmental contaminants in bald eagles in the Columbia river estuary. High levels of DDE, PCBs and TCDD were found in eggs and adults. DDE and PCBs were also found in nestlings indicating early dietary exposure. Mercury levels were higher in adults, indicating accumulation with age. The role of dioxin was unclear, but concentrations in eggs were similar to those found to have deleterious effects in other species in laboratory exposures. Resuspension of dredged sediments played an important role in bioavailability. Eggshell thinning was present and related to DDE and PCBs. DDE and PCB concentrations averaged 9.7 and 12.7 ppm (wet weight) respectively. TCDD concentrations averaged 60 ppt in eggs. Contaminant levels were 2-3 times higher in northern squawfish than in suckers, and both fish are components of eagles' diets. Fish-eating birds were probably the source of DDE, but fish were more likely source of PCBs (tissue concentrations of PCBs in all fish samples exceeded 0.5 ppm - the recommended level for protection of fish-eating birds and mammals). Three of 12 fish samples contained mercury concentrations that exceeded dietary levels shown to interfere with successful reproduction in mallards. Kubiak *et al.* (1989) concluded that PCBs were responsible for embryotoxicity in Forster's tern in Lake Michigan. The TCDD residues in eagle eggs (60 ppt) were higher than concentrations (37 ppt) found to impair reproduction in Forster's terns in Lake Michigan. TCDD levels in prey species averaged 2.8 ppt, 40 times higher than the fish consumption guideline for human health. Elevated concentrations of DDE and PCBs were also found in mink, otter, and black-crowned night herons. A link between fish uptake and dredging of sediment contaminated with PCBs and DDE has been demonstrated (Seelye 1982).

Frenzel and Anthony (1989) found that exposure to environmental contaminants in wintering bald eagles was greatly dependent on the exposure history of the prey item. In many cases, exposure to embedded lead shot in waterfowl constituted the greatest hazard. Organochlorines and mercury were low in voles and jackrabbits. Waterfowl had higher levels of these contaminants, followed by increasing levels in dabbling ducks and diving ducks. The highest concentrations were found in western grebes and California gulls. Dietary exposures of wintering, nesting, and rearing eagles may differ greatly depending on seasonal differences in location and food type.

Wiemeyer *et al.* (1993) reviewed the effect of environmental contaminants on bald eagle productivity. Young production was normal if the eggs contained $< 3.6 \mu\text{g DDE/g}$, was reduced by half between 3.6 and $6.3 \mu\text{g/g}$, and reduced by half again at concentrations $> 6.3 \mu\text{g/g}$. Other contaminants were also associated with poor reproduction, but since they were highly correlated with DDE, it was difficult to assess their individual effects. Concentrations of contaminants appeared to be declining in many parts of country between mid-70s and mid-80s, but specific contaminant(s) varied with location. The data supported the concept of a threshold effect for DDE. The effect of PCBs was less clear, since there are very toxic coplanar congeners that we know relatively little about.

Craig *et al.* (1990) evaluated lead toxicity in golden and bald eagles. Liver concentrations of $\leq 2 \text{ ppm}$ were indicative of uncontaminated birds, 2-8 ppm, sublethally contaminated, and $\geq 8 \text{ ppm}$ acutely contaminated. Uptake of lead was probably not from organisms contaminated from feeding at a lead-contaminated site, but from hunter-killed game, including waterfowl.

Kozie and Anderson (1991) reported that bald eagles nesting on the shores of Lake Superior exhibited lower production than eagles from inland sites in Wisconsin. Contaminant levels were also higher in eagles from Lake Superior sites compared with inland sites. Herring gulls were considered the primary source of contaminants and contained much higher DDE and PCB residues than fish ($5.5 \text{ vs } 0.07 \mu\text{g DDE/g}$ and $16.95 \text{ vs } 0.21 \mu\text{g PCB/g}$ wet weight, respectively). DDE contamination in Lake Superior appeared due primarily to atmospheric sources. In the late 1960s concentrations in fish averaged $0.46 \mu\text{g/g}$ and appear to be declining. Concentrations $\geq 2.8 \mu\text{g DDE/g}$ in diet contributed to reproductive failure in bald eagles.

Mammals

Mink and otter: Mink have been widely used in toxicology as a model species for drug and metabolism studies (Calabrese *et al.* 1992, Bursian *et al.* 1992). They are also widely distributed throughout the Delta where they are one of the top mammalian predators. Consequently, they should reflect contamination frequently associated with a position near the top of the food chain. Calabrese *et al.* (1990) reported that mink are highly sensitive to PCBs.

These authors noted that mink were not particularly sensitive to chlorinated hydrocarbon insecticides, but that adverse effects on growth and reproduction occurred when mink were fed PCB-contaminated fish from the Great Lakes. Elevated methyl mercury concentrations in fish also caused neurological toxicity and dioxin exposure induced wasting syndrome and gastric lesions in mink. Aulerich *et al.* 1990 reported that dietary levels of more than 12.5 mg/kg heptachlor given for 28 days resulted in adverse effects, particularly on growth. This level of sensitivity was considerably greater than for rodents given dietary heptachlor. Consideration should be given to a monitoring program that looks at body burdens in mink to evaluate the potential for adverse effects due to accumulation of xenobiotics.

Ropek and Neely (1993) reported that tissue mercury concentrations were elevated 3-4 times over concentrations in their diet in otters. Mercury was accumulated in both liver and kidney (higher in liver). Males accumulated more than did females. Average levels were 2.2 mg/Kg in liver (dry weight) and 1.5 mg/kg in kidney. Daily dietary levels of 2 ppm methylmercury were lethal within 7 months (O'Connor and Nielsen 1981). Liver levels in otter from polluted areas (Georgia) averaged 7.5 ppm mercury.

Muskrat: Halbrook *et al.* (1993) compared muskrats inhabiting polluted and unpolluted sites. They found that muskrats inhabiting a contaminated waterway exhibited reduced fat indexes and spleen weights, greater adrenal weights, and increased incidence of disease and parasitism compared with those found in relatively uncontaminated sites. Increased body burdens of aluminum, cadmium, copper, nickel, zinc, and polyaromatic hydrocarbon compounds were associated with muskrats collected from the polluted site. Fish from the same waterway also exhibited signs of adverse effects including fin erosion, cataracts, and liver tumors. These data suggest that monitoring program to evaluate tissue concentrations and other indices of contamination in aquatic mammals in the Bay/Delta system would provide useful information on the extent of exposure incurred by these species.

Interactive Effects

Barnthouse *et al.* (1990) evaluated the effect of life history, data uncertainty and exploitation intensity on the potential effects of toxic contaminants on fish. Their evaluation compared the responses of fish with two different life history strategies, gulf menhaden and striped bass.

Ecological theory suggests that species with long life and low reproductive potential, such as striped bass, may be most vulnerable to changes in environment. However, risk assessment also depends on other data including results from different types of toxicity tests, tests on different species (taxonomic distance), and Quantitative Structure Activity Relationships (QSARs). Fishing mortality overlays these effects as it reduces the ability of a population to sustain itself and may be difficult to separate from other causes of mortality. Differences in life history strategy are apparent between the two species: menhaden are short-lived (≤ 5 year) filter feeders, while striped bass are large, long-lived (≥ 10 year) piscivores. Data from populations impacted by power plants suggests a factor of 2 precision in predicting effects on year class abundance of fish population is possible, but this is probably the best we can do. Order of magnitude uncertainty in predicting contaminant mortality is probably more typical. Both test type and taxonomic distance between test species are potentially responsible for significant uncertainty in predicting effects. For example, chronic tests on the species and contaminant of interest provide the greatest accuracy in predicting effects, and fecundity data are important since many toxicants exhibit reproductive effects and fecundity may be the most sensitive endpoint. Conversely, a life cycle test on another species or an LC_{50} on the species of interest increases the uncertainty to factor of 150. LC_{50} estimates on another species or QSAR are virtually useless for risk assessment since the uncertainty factor approaches 300 and may reach almost 3 orders of magnitude for predicting an EC_{10} . The effect of fishing is to further reduce EC_{10} estimates, but only by factors of 6 -10, which are modest compared with the uncertainty of estimating contaminant risk (up to a factor of 300). Modelling indicated that striped bass would be more at risk than menhaden. Important factors usually ignored include potential effects on fecundity, cumulative effects of toxicants on different life stages, effect of life history on the capacity of a population to sustain additional mortality, and the combined effects of multiple stressors.

Marcogliese *et al.* (1992) reported that the composition of the zooplankton community was significantly altered following disruption of a fish community by selenium toxicity. In this case, the piscivorous species in a cooling reservoir were eliminated, leaving only planktivores. Although the total number of species remained similar, the abundance of formerly predominant cladocerans and copepods declined, particularly those > 1 mm in body size. This appeared due to selective feeding by planktivorous fish and loss of refugia for zooplankton in areas of the

reservoir that were formerly dominated by piscivores.

Brazner and Kline (1990) evaluated the effects of chlorpyrifos on the dietary composition and growth of fathead minnows reared in littoral enclosures in a natural pond. Chlorpyrifos was applied once at 0.5, 5.0, and 20.0 $\mu\text{g/L}$. The initial concentrations decreased by approximately 60-80 percent within the first 24 hours after application, but the rate of decay decreased thereafter. At the 0.5 $\mu\text{g/L}$ concentration, the concentration was 0.11 $\mu\text{g/L}$ after 96 hours and < 0.01 $\mu\text{g/L}$ after 384 hours. Effects were apparent in all concentrations. In the lowest concentration, which has the greatest relevance to concentrations found in the Sacramento-San Joaquin watershed, reduced growth was observed 15 days after application (approximately 33 % less than controls). Reduced growth was attributed to reduced numbers of rotifers, cladocerans, immature hydracarina, chironomids, and copepod nauplii compared with untreated ponds. Cladocerans and chironomids decreased by 1 – 2 orders of magnitude in abundance within four days of application. Copepods declined by approximately 50 percent and the response was less dramatic for rotifers. The authors pointed out the possible "costs" of reduced food and growth, including greater vulnerability to predation.

deNoyelles *et al.* (1989) described the effect of atrazine on pond microcosms after 136 and 805 days of exposure. Phytoplankton production and the supported food chain underwent a decrease to 50 percent of the control values, which lasted 3 weeks in duration. A change in species and loss of diversity resulted, with *Chlorophyceae* and *Dinophyceae* being most affected. In contrast, macrophytic communities and the supported food chain remained affected for a much longer period. Fish utilizing a broad spectrum diet showed no adverse effects, but organisms that depended on macrophytes for food and/or cover (tadpoles, bluegill, grass carp, and benthic insect grazers) did poorly. Atrazine's half-life was on the order of several months, and in absence of acquired resistance or tolerance, inhibition of photosynthesis could persist for some time. Grazing stress interacted with pesticide stress to further reduce macrophyte productivity. Tadpole numbers were reduced due to loss of food, loss of substrate for egg deposition, and loss of cover from predation. Benthic grazing insects were reduced through loss of food due to reduced periphyton and macrophyton abundance and bluegill were reduced due to decreases in the number and kinds of insects that served as food organisms. In addition, loss of macrophytes reduced the refugia for bluegill young. Most of the observed

population reductions were caused by indirect effects that would not be identified by laboratory exposures. Thus, field studies can be important tools for determining potential indirect and/or cascading effects of contaminants.

Stewart *et al.* (1992) investigated the effects of macrophytes (*Potamogeton foliosus*) and filamentous algae contaminated with PCBs downstream of the settling basin in which they originated. The plants provided an energy source to the stream reach in which they settled. Snails (*Elimia sp.*) grew more slowly on contaminated vegetation, leachates prepared from contaminated vegetations were toxic to *C. dubia*, and amphipods (*Gammarus sp.*) preferred uncontaminated vegetation for forage. The authors were not able to differentiate between the effects of the energy subsidy and contaminants with respect to the absence of mayflies and stoneflies in the stream reach downstream of the settling basin. In general, aquatic plants can sequester contaminants and cycle them to overlying water. Such contaminants enter the food web through herbivores or detritivores and may be physically released in different forms to the water column as the plants decompose. Zinc, copper, mercury, and nickel were also elevated in the plants to levels of concern.

Waara (1992) examined the effects of copper, cadmium, and lead and zinc on nitrate reduction in synthetic water and lake water, and fifty percent inhibition was found for a mixed heterotrophic culture of bacteria at 25, 85, 95, and 200 µg/L, respectively, in the synthetic medium. In lake water, approximately 25 percent reduction occurred at 10 µg/L copper. Lower pH and phosphorous levels (5.9-6.7 and 10-22 µg/L P, respectively) increased toxicity more than it was reduced by organic content.

DISCUSSION

The data presented herein provide support for the hypothesis that toxic contaminants are present in the Bay/Delta system and associated tributaries at concentrations that are associated with adverse effects. Contaminants elevated to levels of concern include PAHs, PCBs, chlorinate, organophosphorous and carbamate pesticides, various metals and selenium. Sediment and effluent toxicity has been documented as has water column toxicity. Water column toxicity due to pesticides, in particular, is widespread and related to agricultural and urban inputs. Analytical data from hundreds of samples demonstrate that pesticide contamination is widespread and pesticide concentrations frequently exceed water quality criteria intended to protect aquatic life. The historical record suggests that this situation has been on-going. Records from the mid-70s and mid-80s indicate that large quantities of rice pesticides were transported to the Delta. DDT transport from the San Joaquin Valley was also high and concentrations remain above water quality criteria values.

The potential interactions between toxic contaminants and the hydrodynamics of the system are complex. For example, rainfall patterns may move pesticides and other contaminants off-site into receiving waters. Conversely, higher flow rates may tend to dilute toxicants. Because of year-to-year variability, it is difficult to identify dominant factors that affect transport of contaminants which result in toxic concentrations in the receiving water. These problems may have been exacerbated by low flow periods associated with recent droughts and water management policies, particularly since the mid-80s (see changes in flow patterns shown in Figure 1). Data from birds and seals that inhabit the Estuary suggest that contaminant levels in tissues are approaching or have exceeded thresholds for adverse effects.

Direct evidence for toxicity also comes from ambient water samples collected from the Bay/Delta system and tested for toxicity. Dozens of these samples collected over the past five years produced adverse effects on exposed organisms within short (≤ 7 day) exposure times. A broad spectrum of organisms were affected, including fish, algae, mollusks, zooplankton, mysids, and echinoderms. In addition, the preponderance of samples collected from point-source and stormwater discharges also exhibited acute and chronic toxicity.

The presence of toxicity in waters in the system is in direct conflict with the Regional Water Quality Control Boards' narrative objectives of no chronic toxicity in California waters. Given that many of the examples of toxicity are acute responses, the contrast between the objective and current conditions is considerable. Furthermore, the California Department of Fish and Game Code prohibits the presence of toxic substances in toxic amounts in California waters. Given that specific contaminants, notably metals and pesticides among others, have been identified through Toxicity Identification Evaluations as causing toxicity, there would appear to be demonstrated violations of the Code. Pesticides, in particular, have been associated with toxicity under a variety of conditions and locations. This would appear to be a fundamental problem with use practices that result in receiving water concentrations that clearly exceed water quality and toxicity thresholds and one that has not been forcefully addressed under the Code.

EPA (1991) published a technical support document for water-quality based toxicity control. In this document, the Agency provides rationale for the development and application of water quality standards based on toxicity which are designed to protect aquatic communities. For acute toxicity, a maximum 1-hour exposure duration is permitted. For chronic or sublethal effects, the maximum allowable duration is 4 days. EPA estimates that a 3-year period is necessary for impacted communities to recover from perturbations. In other words, for both the acute and chronic criteria, exceedences can only occur once within a 3 year period without disrupting the natural community. Both the frequency and intensity of toxicity described herein suggest that these thresholds are being exceeded in the Bay/Delta system at a frequency that does not permit natural communities time to recover.

Given the difficulty of linking changes in natural populations with contaminants, it is informative to explore the potential for effects in the context of what is known about the organisms and productivity in the Bay/Delta system. From the water quality criteria perspective, pesticide concentrations in this system has exceed criteria values with alarming frequency. These criteria values were calculated from acute and chronic toxicity test data from a wide variety of aquatic species. The assumption is that protecting individual species will also preserve ecological function. However, the criteria are calculated to extend protection to only 90 percent of all possible species (the EPA approach does allow for implementation of more

stringent standards to protect more sensitive species if they are of significant economic or ecological importance). While this approach prevents "over protection", it does not necessarily protect all of the species in the receiving water. Thus, the calculated criteria values should not be considered overly protective or inconsistent with a wide range of species. Consequently, the fact that pesticide concentrations in Bay/Delta and tributary waters regularly exceed the criteria values should be a significant cause for concern. [interestingly, California's Ocean Plan provides guidelines for the development of criteria using the 3 *most* sensitive species].

Similar reasoning applies to the results of bioassays on ambient waters and discharges. EPA guidelines for water quality based toxicity standards indicate that responses from the laboratory test species should be within one order of magnitude of the most sensitive species present in the receiving water (EPA 1991). Thus, while the absence of toxicity in laboratory tests on ambient water samples does not guarantee that the water is non-toxic to members of the natural community, the presence of toxicity in the laboratory tests almost certainly indicates adverse effects on the receiving water organisms. This relationship is based on a number of studies conducted by the EPA and independent investigators that related toxicity to observed instream effects in both fresh and saltwater. These comparisons, which included data from over 200 sites, indicated that adverse effects on the biological community could be predicted on the basis of toxicity in approximately 90 percent of the cases (EPA 1991). More recently, bioassays were shown to be good indicators of effects on community structure in a stream that received agricultural discharge (Crane *et al.* 1995). The high percentage of predictive power, coupled with the diversity of sampling sites, suggests that the relationship between measured toxicity and community effects is robust and should apply to the Bay/Delta system. In this regard, the overall decline of species and productivity in the Bay/Delta system is consistent with the frequent exceedences of the criteria and toxicity standards described herein.

As a point of clarification, the laboratory toxicity tests are applied as a battery to identify the presence of a wide variety of toxicants in the receiving water. For example, fathead minnows are not just a surrogate fish species, but represent a sensitive indicator of ammonia and metal toxicity. However, some fish species are up to 300 times more sensitive to organophosphorous pesticides than fathead minnows, which makes the minnow a poor organism with which to identify the potential for pesticide toxicity to fish. By applying the test battery concept, the presence of these toxicants is indicated by toxicity to *C. dubia*, which

exhibits a higher degree of sensitivity to many different pesticides. Thus, the use of these tests should be regarded collectively as an analytical tool for identifying the presence of toxicants in the receiving water.

In general, specific effects of contaminants have not been demonstrated for a wide range of species that inhabit the Bay/Delta system. This is primarily because many of the species in question are available only on a seasonal basis and laboratory methods have not been developed specifically for them. In addition, it is very difficult to separate sources of mortality in field studies of populations, particularly those that fluctuate in response to environmental stress (Bennett *et al.* in press, Goodyear 1985, Houde 1989).

To strengthen the link between laboratory studies and indigenous species, it is informative to compare results for the laboratory surrogate species *C. dubia* with those from *N. mercedis*, a species widely recognized for its importance to eco-dynamics within the Estuary. Pesticide sensitivities for both species follow:

Pesticide	LC50 ($\mu\text{g/L}$)	
	<i>C. dubia</i>	<i>N. mercedis</i>
chlorpyrifos	0.06	0.07 – 0.08
diazinon	0.4	1.2 – 1.9
carbofuran	2.5	2.7 – 4.7
methyl parathion	2.6	0.20
malathion	2.1	2.2

Data from Bailey *et al.* (accepted), Brandt *et al.* (1993) and Norberg-King *et al.* (1991).

The two species exhibited similar sensitivities to chlorpyrifos and malathion. *C. dubia* were somewhat more sensitive to diazinon and carbofuran, and substantially less sensitive to methyl parathion. Note that most of the differences between the two species fall within the factor of 2, which is the variability generally associated with data from the same laboratory and within the factor of 4, which is the variability generally associated with data obtained on the same chemical from different laboratories. Overall, these data suggest that the two species exhibit similar sensitivities to the pesticides evaluated.

Another data set relevant to this interspecific comparison are the simultaneous exposures with *C. dubia* and *N. mercedis* to samples collected from the Alamo River in the Imperial Valley. This waterway frequently exhibits toxicity that is largely related to agriculture return waters dominated by many of the same pesticides associated with toxicity in Bay/Delta waters (DiGiorgio *et al.* 1995). A total of 99 ambient water samples were tested with both species. Of the 41 samples that exhibited toxicity to *C. dubia*, only 8 (19.5 %) failed to produce acute toxicity to *N. mercedis*. Conversely, 67 of the 99 samples produced toxicity to *N. mercedis*. These data suggested that acute toxicity results obtained with *C. dubia* were indicative of acute toxicity to *N. mercedis* at least 80 percent of the time. Furthermore, based on the greater frequency of toxic responses, *N. mercedis* would appear to exhibit greater sensitivity in general. A similar relationship with sensitivity between *N. mercedis* and *C. dubia* was also found for samples collected from Colusa Basin Drain (Foe and Connor 1991). Collectively, these data suggest that results obtained with *C. dubia* should be applicable to one of the most important organisms found in the Delta.

Given the preceding discussion and data presented, it would appear that toxic contaminants could be associated with major impacts on aquatic organisms in the Bay/Delta system. For this not to be true, the species within the system and system dynamics would have to be unique. This is highly unlikely, given the wide variety of species for which toxic responses have been documented and the robust nature of water quality criteria development. The high predictive power of laboratory studies for water quality based toxicity monitoring, the similarity in responses between *C. dubia* and *N. mercedis*, the relationship between rice pesticides and striped bass recruitment, and the reduced reproductive success of starry flounder collected from sites with contaminated sediments further argue that the measured levels of contaminants and toxicity are likely to adversely affect resident organisms. These observations are consistent with widespread declines in aquatic organisms in the system.

With respect to aquatic avian and mammalian species, the available data indicate that several persistent pollutants that tend to concentrate at the top of the food web, including selenium, mercury, PCBs, and DDE, are at or above their thresholds for toxic effects, especially in birds where most of the data are available. Since no major changes in the management of sources of selenium and mercury have been made in recent years, concentrations of these elements

probably will remain high in the Estuary. Although the use of DDT was banned more than 20 years ago, residues of DDT and its metabolites are still circulating through the system due to their extreme persistence, mobilization from sediment, and probably also to continuing inputs from the watershed. Sale of PCBs was also banned in the 1970's, but these compounds are still abundant in the Estuary due to their persistence, atmospheric sources, remobilization from sediment, and continuing inputs from the watershed. It is estimated that 60% of the total quantity of PCBs manufactured are still in use (Rice and O'Keefe, 1994).

With the exception of the Great Lakes, this summary probably represents the largest body of data characterizing a contaminated aquatic ecosystem in the United States. Observations of high body burdens, exceedences of water quality criteria, and toxicity in ambient water samples are consistent with an adversely impacted system. This observation is supported by dramatic declines in fish and invertebrate populations. Failure of regulatory agencies to address this problem, which is probably second only to water inflow issues in terms of importance to maintaining a healthy Bay and Delta, will likely reduce the effectiveness of any plan to restore the health of the Estuary. Consequently, it would seem irresponsible not to consider the effects, interactions, and elimination of toxic levels of pollutants in any program aimed at the recovery of the Bay/Delta system.

CONCLUSIONS AND RECOMMENDATIONS

Ambient Toxicity and Monitoring Programs

Conclusion: *Toxicity in water samples collected from the Estuary and associated watersheds is frequent and widespread.*

Recommendations:

- ☐ Continue monitoring to establish relationships between contaminants, sources and use patterns.
- ☐ Maintain monitoring at frequent intervals to identify intermittent but potentially significant toxic events.
- ☐ Increase monitoring intensity in high value habitats (nursery areas, for example) such as the smaller drainages into the Delta and "dead end" sloughs (upper end of Suisun Marsh, for example). These areas are most susceptible to local water diversions, and agricultural and stormwater impacts.
- ☐ Implement an aggressive ambient water quality monitoring program in the Bay similar to that in operation in the Delta.

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Conclusion: *The most notable response in the toxicity tests on ambient waters was the acute mortality seen with the invertebrates. However, effects were also frequently observed with the fish and algae.*

Recommendations:

- ☐ Continue monitoring with the suite of species to identify different contaminants.
- ☐ Continue to investigate the cause of toxicant-induced mortality and growth effects

with fathead minnows. The effects of reduced growth on year-class strength has been widely documented with many fish species, whether due to reduced forage base, adverse environmental conditions or, in this case, toxicants.

- ☐ Continue to investigate causes of reduced growth in algae; reduced primary productivity is of concern in any ecosystem.

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Conclusion: *Regional Board monitoring data suggests toxic contaminants were observed in elevated concentrations in the North Bay and South Bay.*

Recommendations:

- ☐ Undertake a sampling program in the Napa River, Petaluma River and Sonoma Creek drainages to determine the presence and degree of agricultural and other contaminants in these watersheds.
- ☐ Evaluate stormwater and POTW contributions of metals and other contaminants to the South Bay. Identification of sources will strongly influence control measures.

Agricultural Inputs

Conclusion: *The widespread finding of pesticides in receiving waters at concentrations that exceed acute and chronic water quality criteria and no-effect levels suggests that current regulatory and monitoring activities are inadequate to protect receiving water quality.*

Recommendations:

- ☐ Revise requirements for pesticide registration packages to include data that will provide sufficient understanding of the environmental fate of particular chemicals to allow identification of such problems before they occur.
- ☐ Increase the scope of analytical monitoring to ensure that required pesticide usage patterns are effective in maintaining concentrations of pesticides and their degradation

products in the receiving waters below those that cause adverse effects.

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Conclusion: *Increased regulatory controls have effectively reduced or eliminated acute toxicity from rice, the largest single source of agricultural water returned to the system.*

Recommendations:

- ☐ Continue monitoring to ensure compliance; in 1993 non-compliance releases from < 3 percent of the total acreage devoted rice culture resulted in 20 – 50 fold increases in mass loadings of rice pesticides to the Sacramento River.
- ☐ Continue to aggressively ensure that objectives and water quality criteria for associated pesticides are met.

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Conclusion: *Recent evidence suggests that toxicity to invertebrates can be largely attributed to carbofuran, diazinon and chlorpyrifos. Methidathion, malathion and methyl parathion have also been implicated.*

Recommendations:

- ☐ Identify crops and application practices that facilitate entry of these insecticides into receiving waters.
- ☐ Develop best management plans for these pesticides that reduce application rates, increase dissipation and degradation rates, or otherwise prevent their presence in receiving waters at toxic concentrations. Our experience with rice suggests that substantial reductions in receiving water concentrations can be made with minimal impact on growers.
- ☐ Investigate environmental factors that facilitate the presence of pesticides in receiving waters at toxic concentrations. Clearly, information submitted with the registration packages for the chemicals in question was inadequate for the purposes of assessing

the likelihood of exceeding environmentally acceptable concentrations. For example, if dissipation rates were controlled by temperature and the rates were calculated based on data obtained at 15–25°C, the half-life would be considerably longer if the material were applied in the winter at an average temperature of 10–12 °C.

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Conclusion: *New chemicals may be introduced to replace ones identified as causing adverse effects on water quality. One problem should not be traded for another.*

Recommendations:

- ☐ The performance of substitute chemicals with respect to their ability to reach toxic concentrations in the receiving waters under the same use conditions as the chemicals they replace needs to be rigorously evaluated *prior* to their introduction on a widespread basis.

Urban Stormwater Inputs

Conclusion: *Seasonal inputs of stormwater from urban and agricultural sources are consistently toxic.*

Recommendations:

- ☐ Continue efforts to identify toxicants and sources.
- ☐ Identify patterns that predispose toxic contaminants to enter stormwater run-off so that source control measures can be taken.
- ☐ Investigate ways to manage or treat stormwater; seasonal marshes or wetlands may have promise in this application.

Point Source Inputs

Conclusion: *The effluent characterization program implemented by Region II is the best example of this type of program to date.*

Recommendation:

- ☐ Implement this type of program more fully for dischargers in other parts of the Estuary.

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Conclusion: *The Region II program appears to be lacking in focus and direction at the present. Clearly, if the the EPA estimate of a 3 year period of recovery for toxic exceedences is correct, then increased and continued vigilance is necessary to continue to improve and maintain water quality in the Estuary.*

Recommendations:

- ☐ Implement chronic limits (testing) to all dischargers at a frequency sufficient to serve the purpose of realistically assessing effluent quality. Clearly, testing at intervals of 2–4 times per year is insufficient given the continuous nature and variability of most discharges. Multiple species also need to be incorporated into any testing requirements.
- ☐ Maintain high frequency of testing to identify and treat intermittent toxicity events as they occur. Even considering monthly testing at an estimated cost burden of \$3000 per month, this equates to only \$0.005 per gallon per month for a 20,000 gal/day discharger. For a 1 mgd discharger, the cost would be less than \$0.0001 per gallon per month. These are, by far, the least expensive alternatives for disposing of wastewater, arguably a “drop in the bucket”.
- ☐ Aggressively pursue TIEs, treatment methodologies and source control strategies to remove toxicity.
- ☐ Increase aggressive enforcement activities, not only with respect to penalties, but especially to reduce the time that exceedences are allowed to continue without abatement.

Sediments

Conclusion: *Evidence suggests that sediments are contaminated at least on local basis.*

Recommendations:

- ☐ Investigate extent of adverse effects on biological productivity in contaminated areas.
- ☐ Assess bioavailability and mitigation plans, if warranted, for areas identified.
- ☐ Consider impacts of dredging in contaminated areas with respect to resuspending or otherwise increasing the bioavailability of contaminants. Similarly, disposal to flooded islands and levees should be done in ways consistent with minimizing resuspension or solubilization of contaminants associated with the sediment phase.

Species

Conclusion: *All three test species responded to ambient water samples, suggesting the presence of multiple toxicants.*

Recommendation:

- ☐ Continue testing efforts to identify toxicants and relationships to seasonal patterns.

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Conclusion: *Data suggest that fathead minnows may be relatively insensitive to a variety of toxicants compared with other fish species.*

Recommendation:

- ☐ Consider adding another fish species to the suite of bioassay species. Some of the species, particularly those that are indigenous to the system may only be available seasonally in the early life stages.

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Conclusion: *EPA data strongly suggest that toxicity reported herein should be indicative of adverse effects in the Estuary's waters. In addition, work on some of the local species (e.g., striped bass and Neomysis) suggests that toxicants are, or have been, associated with impacts on these species. However, studies relating contaminants to population declines of many species in the Estuary are lacking.*

Recommendations:

- ☐ Conduct additional studies to determine sensitivity of indigenous algal, invertebrate and fish species to assess what role, if any, contaminants may have played in affecting declines of species either through direct toxicity or through reductions in food supply.
- ☐ Evaluate differences in sensitivity to selected toxicants that might favor introduced species at the expense of historically occurring species.
- ☐ The use of *in situ* exposures with indigenous organisms may provide useful data on interactions between local hydrology and contaminants.

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Conclusion: *Regional Board monitoring efforts of tissue concentrations of contaminants has largely focused on human health hazards by evaluating concentrations of contaminants in fish filets. In addition, tissue concentrations in the top avian and mammalian predators have been largely ignored; these species are where the effects of accumulated contaminants will be most apparent.*

Recommendations:

- ☐ Incorporate monitoring of tissue levels of organisms at high end of food chain – cormorants, gulls, seals, otters, mink, etc. – into program.
- ☐ Monitor biomarkers and concentrations in tissues such as liver and gonad to evaluate

exposure history and determine, through comparisons with the literature and comparative studies, if body burdens are at high enough levels to affect the organism.

- ☐ Include within such studies a program to look at effects of "estrogen mimics". Reproductive impairment will most likely be apparent at the highest trophic levels.
- ☐ Since many of these contaminants have their most severe effects on avian reproduction, further study of body burdens and reproductive effects would be in order to characterize effects on bird populations.

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Conclusion: *Adverse effects have been observed in other large aquatic ecosystems that have been due to contaminants for which we have little data on their effects in the Estuary.*

Recommendations:

- ☐ Compare tissue concentrations of selenium, mercury, PCBs, PAHs and DDTs in representative organisms from the Estuary to those associated with adverse effects in the Great Lakes and other environments to determine the level of concern for a similar situation to occur here.
- ☐ Compare aqueous TBT concentrations to determine if this material poses a problem the Estuary.

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APPENDIX A

Delta Sampling Sites

Delta Sampling Sites.

Major inputs to the Delta

Sacramento river at Hood
Mokelumne river at New Hope Rd.
San Joaquin river at Vernalis

Smaller creeks and sloughs

Ulatis creek
French Camp slough
Duck slough
Lindsey slough
Prospect slough
Snodgrass slough
Paradise Cut

Island Drains

Ryer Island Main Drain
Twitchell Island Main Drain
Bouldin Island Main Drain
Victoria Island Main Drain
Pierson District Main Drain

Urban run-off dominated area

Port of Stockton

Pathways of water through the Delta

Sacramento river at Rio Vista
Old river at Highway 4
Old river at Tracy Blvd.
Middle river at bullfrog
Middle river at Tracy Blvd.
Delta Mendota Canal

APPENDIX B

Summary of Toxicity Associated with Point-Source Dischargers and Ambient Water in the San Francisco Bay Region

Summary of Toxicity Associated with Point-Source Dischargers

Discharger	Type	Flow (mgd) in 1994	Dilution	Acute Toxicity	Chronic Toxicity	Ambient Toxicity
East Bay Municipal Utility District	Municipal	72.4	1:10	18/18- <i>C. dubia</i> 15/18- <i>M. beryllina</i>	0/11- <i>C. dubia</i> 1/18- <i>M. beryllina</i> 4/11-echinoderm	not reported
San Jose/Santa Clara	Municipal	113.0	none	2/19- <i>C. dubia</i> 0/19- <i>M. beryllina</i>	5/19- <i>C. dubia</i> 1/19- <i>M. beryllina</i> 2/15-diatom	4/8- <i>M. beryllina</i> ; South Bay
Chevron USA	Refinery	4.9	1:10	4/11- <i>M. beryllina</i>	8/11- <i>M. beryllina</i> 1/6-echinoderm 1/7-bivalve	not reported
Shell Oil Company	Refinery	4.3	1:10	14/17- <i>P. promelas</i> 13/15- <i>M. bahia</i> 8/16- <i>C. dubia</i>	2/17- <i>P. promelas</i> 3/15- <i>M. bahia</i> 9/16- <i>C. dubia</i>	not reported
USS POSCO	Steel Mill	8.7	none	1/11- <i>C. dubia</i> 2/12- <i>M. beryllina</i>	6/12-echinoderm 3/11- <i>C. dubia</i> 2/12- <i>M. beryllina</i>	6/12-echinoderm 11/11- <i>C. dubia</i> 2/12- <i>M. beryllina</i> ; New York Slough
City of San Francisco SE Plant	Municipal	71.6	1:10	9/10- <i>C. dubia</i> 8/9- <i>M. beryllina</i> 8/8-sanddab	8/10- <i>C. dubia</i> 1/9- <i>M. beryllina</i> 1/3-echinoderm 7/10-bivalve	not reported

Summary of Toxicity Associated with Point-Source Dischargers

Discharger	Type	Flow (mgd) in 1994	Dilution	Acute Toxicity	Chronic Toxicity	Ambient Toxicity
City of Benicia Wastewater Treatment Plant	Municipal	2.4	1:10	12/14- <i>P. promelas</i> 14/17- <i>M. bahia</i>	3/17- <i>P. promelas</i> 9/17- <i>M. bahia</i> 8/9-echinoderm	1/9-echinoderm; Carquinez Strait
Delta Diablo Sanitation District	Municipal	11.5	1:10	4/18- <i>M. bahia</i> 12/18- <i>M. beryllina</i>	4/17- <i>M. bahia</i> 6/18- <i>M. beryllina</i> 10/18-echinoderm	not reported
Vallejo Sanitation and Flood Control District	Municipal	12.2	1:10	1/18- <i>P. promelas</i> 10/18- <i>M. bahia</i> 12/18- <i>C. dubia</i>	0/18- <i>P. promelas</i> 5/17- <i>M. bahia</i> 4/18- <i>C. dubia</i>	not reported
San Francisco: North Bayside System Unit	Municipal	16.6	1:10	7/16- <i>M. beryllina</i> 10/16- <i>M. bahia</i>	1/16- <i>M. beryllina</i> 7/16- <i>M. bahia</i> 2/16-echinoderm	2/16-echinoderm
Napa	Municipal	10.5	none	0/9- <i>C. dubia</i> 0/9- <i>P. promelas</i>	4/9- <i>C. dubia</i> 4/9- <i>P. promelas</i> 7/9-echinoderm	4/9-echinoderm; Napa River
PG&E Pittsburg Power Plant	Cooling	613.0	none	0/6 <i>M. beryllina</i>	1/6- <i>M. beryllina</i> 2/6-diatom 4/6-echino:bivalve	2/6-diatom 2/3-bivalve 3/3-echinoderm

Summary of Toxicity Associated with Point-Source Dischargers

Discharger	Type	Flow (mgd) in 1994	Dilution	Acute Toxicity	Chronic Toxicity	Ambient Toxicity
PG&E Potrero Power Plant	Cooling	199.0	none	2/6- <i>M. beryllina</i>	1/6- <i>M. beryllina</i> 2/6-diatom 2/4-bivalve 0/1-echinoderm	1/6- <i>M. beryllina</i> 4/6-diatom 3/4-bivalve 0/1-echinoderm; Potrero Point
General Chemical	Industrial	0.52	1:10	0/7- <i>M. beryllina</i>	1/7- <i>M. beryllina</i> 2/6- <i>C. dubia</i> 1/5-bivalve 0/2-echinoderm	1/2- <i>M. beryllina</i> 1/2-bivalve; Suisun Bay
Exxon	Refinery	2.0	1:10	4/16-Microtox 14/16- <i>M. bahia</i>	1/16-echinoderm 2/14- <i>M. bahia</i>	not reported
DOW Chemical Company	Industrial	0.34	1:10	1/17- <i>P. promelas</i>	3/17- <i>P. promelas</i> 8/19-diatom 10/14-echinoderm 1/4-bivalve	8/19-diatom
San Mateo	Municipal	11.8	1:10	3/19- <i>P. promelas</i> 7/18- <i>M. bahia</i> 0/17- <i>C. dubia</i>	3/17- <i>P. promelas</i> 6/20- <i>M. bahia</i> 3/17- <i>C. dubia</i>	not reported

Summary of Toxicity Associated with Point-Source Dischargers

Discharger	Type	Flow (mgd) in 1994	Dilution	Acute Toxicity	Chronic Toxicity	Ambient Toxicity
Petaluma	Municipal	5.4	none	1/5- <i>M. bahia</i> 0/4- <i>M. beryllina</i>	3/5- <i>M. bahia</i> 2/3- <i>M. beryllina</i> 4/4- <i>S. capricornutum</i>	not reported
Las Gallinas	Municipal	2.7	none	0/4- <i>C. dubia</i> 2/3- <i>M. bahia</i>	3/4- <i>C. dubia</i> 3/5- <i>S. capricornutum</i> 2/3- <i>M. bahia</i>	not reported
City of Sunnyvale	Municipal	12.5	none	1/8- <i>C. dubia</i> 0/4- <i>N. mercedis</i>	1/8- <i>C. dubia</i> 1/8- <i>S. capricornutum</i> 1/5-echinoderm	not reported
Central Contra Costa Sanitary District	Municipal	34.8	1:10	15/16- <i>C. dubia</i> 0/16- <i>M. beryllina</i> 2/4- <i>N. mercedis</i>	2/18- <i>C. dubia</i> 1/17- <i>M. beryllina</i> 11/20-echinoderm	not reported
EBDA	Municipal	58.7	1:10	10/17- <i>M. beryllina</i> 11/18- <i>P. promelas</i> 7/11- <i>C. dubia</i>	2/17- <i>M. beryllina</i> 3/18- <i>P. promelas</i> 5/11- <i>C. dubia</i> 3/4-bivalve	only 53% survival in one receiving water sample with <i>M. beryllina</i>
Fairfield Suisun	Municipal	9.7	none	0/6- <i>C. dubia</i> 0/5- <i>M. beryllina</i>	1/6- <i>C. dubia</i> 1/5- <i>M. beryllina</i> 4/6- <i>S. capricornutum</i> 1/2-diatom	not reported

Summary of Toxicity Associated with Point-Source Dischargers

Discharger	Type	Flow (mgd) in 1994	Dilution	Acute Toxicity	Chronic Toxicity	Ambient Toxicity
City of Palo Alto	Municipal	22.4	none	0/15- <i>M. beryllina</i> 0/13- <i>M. bahia</i>	1/15- <i>M. beryllina</i> 0/13- <i>M. bahia</i> 1/2-echinoderm 4/13- <i>S. capricornutum</i> 0/1-bivalve	not reported
West County Agency	Municipal	14.8	1:10	0/18- <i>M. beryllina</i>	1/18- <i>M. beryllina</i> 7/18-echinoderm 13/20-abalone	not reported
C & H Sugar	Cooling	14.0	1:10	not reported	0/4-diatom 1/3-abalone 0/4-echinoderm	1/4-diatom 1/3-abalone 1/4-echinoderm
South Bayside System Authority	Municipal	2.9	1:10	0/9- <i>C. dubia</i> (only 50 percent effluent tested)	2/9- <i>C. dubia</i> 2/8-echinoderm 0/7-diatom	1/7-diatom
North San Mateo County Sanitation District	Municipal	8.1	1:49	not reported	9/13-diatom 12/17-echinoderm 13/14-kelp	not reported
TOSCO Avon	Refinery	4.7	1:10	4/18- <i>M. beryllina</i> 1/18- <i>C. dubia</i> 3/18- <i>P. promelas</i>	1/18- <i>M. beryllina</i> 0/18- <i>C. dubia</i> 0/18- <i>P. promelas</i>	not reported

Summary of Toxicity Associated with Point-Source Dischargers

Discharger	Type	Flow (mgd) in 1994	Dilution	Acute Toxicity	Chronic Toxicity	Ambient Toxicity
Central Marin Sanitary District	Municipal	9.6	1:10	1/18- <i>C. dubia</i> 2/17- <i>P. promelas</i>	3/18- <i>C. dubia</i> 6/17- <i>P. promelas</i> 8/19-diatom	not reported
Novato Sanitary District	Municipal	5.6	none	3/3- <i>M. bahia</i> 1/5- <i>C. dubia</i>	3/3- <i>M. bahia</i> 3/5- <i>C. dubia</i> 2/5- <i>S. capricornutum</i>	not reported

Comments:

Toxicity data from Pacific Refining Company (Hercules, California) was also reviewed. However, the data set was incomplete and subsequently omitted from this summary.

D-001420

APPENDIX C

**Applications of Selected Pesticides Applied to Rice and Flows in the Sacramento River
1970 – 1985 (molinate and thiobencarb) and 1970 – 1988 (carbofuran and methylparathion)**

Table 1. Applications of molinate and thiobencarb and Sacramento River flows at Grimes for the years 1970-1985.

<u>Year</u>	<u>Application (lbs. X 1000)</u>		<u>River Flow (cfs X 1000)</u>
	<u>Molinate</u>	<u>Thiobencarb</u>	
1970	490	na	7.0
1971	797	na	14.9
1972	656	na	8.2
1973	601	na	8.9
1974	457	na	12.7
1975	962	na	15.0
1976	760	na	8.4
1977	598	na	5.7
1978	1300	na	10.0
1979	1400	na	6.7
1980	1600	8	5.6
1981	1700	287	6.9
1982	1500	675	14.0
1983	930	351	23.1
1984	1500	353	6.7
1985	1100	475	5.4

na = not applied.

Table 2. Applications of carbofuran and methyl parathion and Sacramento River flows at Grimes for the years 1970-1988.

<u>Year</u>	<u>Carbofuran</u>	<u>Methyl Parathion</u>	<u>River Flow (cfs X 1000)</u>
1970	9	15	7.0
1971	9	30	14.9
1972	8	23	8.2
1973	11	32	8.9
1974	10	24	12.7
1975	5	23	15.0
1976	9	20	8.4
1977	21	17	5.7
1978	18	45	10.0
1979	29	67	6.7
1980	82	87	5.6
1981	108	100	6.9
1982	116	102	14.0
1983	73	54	23.1
1984	88	74	6.7
1985	58	48	5.4
1986	57	49	6.3
1987	57	57	6.9
1988	59	71	7.5